SUPPORTING INFORMATION FOR

Cobalt(III) Werner Complexes with 1,2-Diphenylethylenediamine Ligands: Readily Available, Inexpensive, and Modular Chiral Hydrogen Bond Donor Catalysts for Enantioselective Organic Synthesis

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⑤ EXPERIMENTAL SECTION

General Data. NMR spectra were recorded on a Varian NMRS 500 MHz spectrometer at ambient probe temperatures. Chemical shifts (δ in ppm) were referenced to residual solvent signals (^{1}H: $CHCl_3$, 7.26; DMSO-d_5, 2.50; CHD_2OD, 3.30; $CDHCl_2$, 5.32; acetone-d_5, 2.05; ^{13}C: $CDCl_3$, 77.2; DMSO-d_6, 39.5; CD_3OD, 49.0; CD_2Cl_2, 54.0; acetone-d_6, 29.8). IR spectra were recorded on a Shimadzu IRAffinity-1 spectrometer (Pike MIRacle ATR system, diamond/ZnSe crystal). UV-visible spectra were obtained with a Shimadzu UV-1800 UV spectrometer. Optical rotations were measured with a Rudolph Autopol II Automatic Polarimeter. Melting points were determined using an OptiMelt MPA 100 instrument. Microanalyses were conducted by Atlantic Microlab. HPLC analyses were carried out with a Shimadzu instrument package (pump/autosampler/detector LC-20AD/SIL-20A/SPD-M20A).

NMR solvents (Cambridge Isotopes) were treated as follows unless noted: DMSO-d_6, distilled under vacuum and stored over molecular sieves; $CDCl_3$, CD_2Cl_2, acetone-d_6, and CD_3OD, stored over molecular sieves. HPLC solvents (hexanes, Fischer; isopropanol, JT Baker; both HPLC Grade) were degassed before use. Other solvents were treated as follows: DMSO (Fischer, ACS grade), distilled under vacuum and stored over molecular sieves; CH_2Cl_2 (EMD Chemicals, ACS grade), CH_3OH (EMD, anhydrous, 99.8%), hexanes (Macron, ACS grade), EtOAc (Macron, ACS grade), and acetone (BDH, ACS grade), used as received unless noted.

Reactions were conducted under air unless noted. Chemicals were treated as follows. The *trans*-β-nitrostyrene (**4a**, Alfa Aesar, 98%) was column chromatographed (silica gel, 9:1 v/v hexanes/EtOAc). The *trans*-4-methoxy-β-nitrostyrene (**4d**), 3,4-dichloro-β-nitrostyrene (**4e**), and 1-(2-furyl)-2-nitroethylene (**4k**) were used as received from Alfa Aesar (NMR showed **4e,k** to be >98% *trans*). Other previously reported nitroolefins (**4b-c**, **4f-g**, **4j**, **4l**; see Scheme 4) were prepared by Henry reactions of nitromethane and the corresponding aldehydes.[s1] Dimethyl malonate (**5c**, Alfa Aesar, 98%), diethyl malonate (**5b**, Alfa Aesar, 99%), diisopropyl malonate (**5a**, TCI, 99%), $Co(OAc)_2{\cdot}4H_2O$ (Alfa Aesar, 98%), $Co(ClO_4)_2{\cdot}6H_2O$ (Alfa Aesar, reagent grade), (*S*,*S*)-dpen ((*S*,*S*)-**2**, dpen = 1,2-diphenylethylenediamine, Oakwood or Combi-blocks), (*R*,*R*)-**2**,

(Oakwood), activated charcoal (Acros, Norit SX 4), $HClO_4$ (70%, Macron, ACS grade), Ag^+ BF_4^- (Aldrich, 98%), Ag^+ PF_6^- (Strem, 99%), *trans*-2-(2-nitrovinyl)phenol (Aldrich, 97%), di-*t*-butyl azodicarboxylate (**7**, Aldrich, 98%), ethyl 2-oxocyclopentanecarboxylate and 2-oxocyclohexanecarboxylate (**8a**,**b**, Aldrich, 95%), acetyl chloride (Aldrich, 98%), benzoyl chloride (Aldrich, 99%), Et_3N (Alfa Aesar, 98%), *N*-methyl morpholine (Alfa Aesar, 99%), DOWEX 50WX2 (Aldrich), silica gel (Silicycle SiliaFlash® F60), Celite 545 (Aldrich), and Na_2SO_4 (EMD) were used as received. The Na^+ BAr_f^- was prepared by a literature procedure (BAr_f^- = B(3,5-C_6H_3-$(CF_3)_2)_4^-$).[s2]

Λ-[Co((*S*,*S*)-dpen)$_3$]$^{3+}$ 3Cl$^-$ (Λ-(*S*,*S*)-3^{3+} 3Cl$^-$; Scheme 1, step A).[s3-s5] A gas circulating flask was charged with a solution of $Co(OAc)_2{\cdot}4H_2O$ (0.296 g, 1.19 mmol) in CH_3OH (50 mL). Activated charcoal (0.1 g) and (*S*,*S*)-**2** (0.849 g, 4.00 mmol, 3.36 equiv) were added with stirring. Air was passed through the vigorously stirred suspension. After 17 h, the mixture was filtered through Celite and aqueous HCl (1.5 mL, 12.0 M) was added. The solvent was removed by rotary evaporation to give an orange solid. A portion was dissolved in CD_3OD. A $^{13}C\{^1H\}$ NMR spectrum showed CHPh signals at δ 63.5, 66.1, and 66.7 ppm (67/10/23), which were attributed to the Λ and Δ diastereomers of (*S*,*S*)-**3**$^{3+}$ 3Cl$^-$, and *trans*-[Co((*S*,*S*)-dpen)$_2$(Cl)$_2$]$^+$ Cl$^-$,[s6] respectively.[s7] Then H_2O (100 mL) was added. The suspension was filtered and the orange filter cake was washed with H_2O (100 mL). The cake was dissolved in CH_3OH. The solvent was removed by rotary evaporation and the residue dried by oil pump vacuum (room temperature, 14 h) to give Λ-(*S*,*S*)-**3**$^{3+}$ 3Cl$^-{\cdot}3H_2O$ as an orange solid (0.662 g, 0.773 mmol, 65%), mp 220-230 °C dec (green liquid; open capillary). The $^{13}C\{^1H\}$ spectrum showed only one CHPh signal, indicative of the Λ diastereomer, as confirmed crystallographically (below). Anal. Calcd. for $C_{42}H_{48}Cl_3CoN_6{\cdot}3H_2O$ (856.21): C 58.92, H 6.36, N 9.82; found C 58.95, H 6.46, N 9.68.

NMR (10:1 v/v DMSO-d_6/CD_3OD, δ in ppm):[s8] ^1H (500 MHz) 7.65-7.42 (m, 12H, *o*-Ph), 7.41-7.15 (m, 18H, *m*-, *p*-Ph), 6.86 (br s, 6H, N**H**H'), 5.31 (br s, 6H, NH**H'**), 4.97 (s, 6H, C**H**NH_2), 4.06 (br s, 10H, CD_3O**H**/**H**$_2O$);[s9-s10] $^{13}C\{^1H\}$ (125 MHz) 137.3 (s, *i*-Ph), 128.9 and 128.8 (2 s, *o*-, *m*-Ph), 128.6 (s, *p*-Ph), 61.8 (s, C**H**NH_2).

Δ-[Co((*S*,*S*)-dpen)$_3$]$^{3+}$ 3ClO$_4^-$ (Δ-(*S*,*S*)-3^{3+} 3ClO$_4^-$; Scheme 1, step B).[s4a,s11] *This synthesis involves the use and preparation of perchlorate salts that are potentially explosive.*[s12] *Although no mishaps occurred, special care and protection are always required when working with perchlorate salts or HClO$_4$ solutions.* A gas circulating flask was charged with a solution of Co(ClO$_4$)$_2$·6H$_2$O (0.261 g, 0.711 mmol) in CH$_3$OH (50 mL). Activated charcoal (0.1 g) and (*S*,*S*)-**2** (0.505 g, 2.38 mmol, 3.31 equiv) were added with stirring. Air was passed through the vigorously stirred suspension. After 17 h, the mixture was filtered through Celite and HClO$_4$ (2.0 mL, 35% in H$_2$O) was added. The solvent was removed by rotary evaporation to give an orange solid. A portion was dissolved in CD$_3$OD, and a ^{13}C{^{1}H} NMR spectrum showed **C**HPh signals at δ 63.6 and 61.8 ppm (92/8). These were attributed to the Δ and Λ diastereomers of (*S*,*S*)-**3**$^{3+}$ 3ClO$_4^-$. The solid was washed with water and dissolved in CH$_3$OH. The solvent was removed by rotary evaporation to give crude (*S*,*S*)-**3**$^{3+}$ 3ClO$_4^-$ as an orange powder (0.422 g, 0.425 mmol, 60%) and an 83:17 mixture of Δ/Λ isomers,[s11] as assayed by ^{13}C{^{1}H} NMR (δ, DMSO-d_6, 63.2/61.4 ppm).[s13] Diastereomerically pure Δ-(*S*,*S*)-**3**$^{3+}$ 3ClO$_4^-$ was obtained per Scheme 1, step D (below).

Data for Δ-(*S*,*S*)-**3**$^{3+}$ 3ClO$_4^-$. NMR (CD$_3$OD, δ in ppm):[s8] ^{1}H (500 MHz) 7.41-7.37 (m, 12H, *o*-Ph), 7.34-7.30 (m, 18H, *m*-, *p*-Ph), 4.89 (br s, 26H, CD$_3$O**H**/**H**$_2$O),[s9] 4.52 (s, 6H, C**H**-NH$_2$);[s15] ^{13}C{^{1}H} (125 MHz): 136.5 (s, *p*-Ph), 130.4 (s, *i*-Ph), 130.0 and 129.0 (2 s, *o*-, *m*-Ph),[s16] 66.5 (s, C**H**NH$_2$).

Λ-[Co((*S*,*S*)-dpen)$_3$]$^{3+}$ 3ClO$_4^-$ (Λ-(*S*,*S*)-3^{3+} 3ClO$_4^-$; Scheme 1, step C).[s4a,s14] A beaker was charged with Λ-(*S*,*S*)-**3**$^{3+}$ 3Cl$^-$·3H$_2$O (0.502 g, 0.0.586 mmol) and boiling CH$_3$OH (200 mL). Then NaClO$_4$ (ca. 0.765 g, 6.25 mmol) was added with stirring, followed by warm water (400 mL). The solution was kept at 0 °C. After 7 h, the yellow precipitate was collected, washed with water, dried by oil pump vacuum at room temperature, and dissolved in a minimum of hot acetone. Ten volumes of ethanol were added. Ether was slowly added, initiating precipitation. More ether was added, and the mixture was kept at 0 °C. After 14 h, the orange solid was collected by filtration and dried by oil pump vacuum at room temperature to give Λ-(*S*,*S*)-**3**$^{3+}$ 3Cl-

O_4^-·$4H_2O$ (0.401 g, 0.376 mmol, 64%).[s4a,s14]

NMR (CD_3OD, δ in ppm):[s8] ^1H (500 MHz) 7.41 (br s, 12H, *o*-Ph), 7.35 (br s, 18H, *m*-, *p*-Ph), 4.88 (br s, 24H, CD_3O**H**/**H**$_2O$),[s9] 4.81 (s, 6H, C**H**NH_2);[s15] $^{13}C\{^1H\}$ (125 MHz): 136.4 (s, *i*-Ph), 130.5 (s, *p*-Ph), 130.3 and 129.7 (2 s, *o*-, *m*-Ph),[s16] 63.7 (s, C**H**NH_2).

Δ-[Co((*S*,*S*)-dpen)$_3$]$^{3+}$ 3Cl$^-$ (Δ-(*S*,*S*)-3^{3+} 3Cl$^-$). A (Scheme 1, step E with diastereomer mixture). A beaker was charged with the 83:17 mixture of Δ/Λ diastereomers of (*S*,*S*)-**3**$^{3+}$ $3ClO_4^-$ obtained above (0.302 g, 0.304 mmol) and CH_3OH (50 mL). The solution was sorbed onto a Dowex cation exchange column (3.0 × 12 cm), giving an orange band. The column was washed with H_2O/CH_3OH (1:1 v/v, 100 mL) and eluted with increasing concentrations of 12.0 M aq. HCl in CH_3OH (9:1 v/v CH_3OH/HCl (100 mL), 8:2 v/v CH_3OH/HCl (100 mL), 7:3 v/v CH_3OH/HCl (100 mL), 6:4 v/v CH_3OH/HCl (until product elution)). An orange band was collected and the solvents were removed by rotary evaporation (45 °C bath; base trap to scavenge HCl). This gave (*S*,*S*)-**3**$^{3+}$ 3Cl$^-$ (0.227 g, 0.283 mmol, 93%) as a bright orange solid and a 83:17 mixture of Δ/Λ isomers, as assayed by $^{13}C\{^1H\}$ NMR (δ, 63.7/62.0 ppm).[s13] **B (Scheme 1, step E with Δ diastereomer).** A beaker was charged with Δ-(*S*,*S*)-**3**$^{3+}$ $3ClO_4^-$ (0.200 g, 0.202 mmol; see below) and CH_3OH (50 mL). The solution was sorbed onto a Dowex cation exchange column. A workup identical to that in A gave Δ-(*S*,*S*)-**3**$^{3+}$ 3Cl$^-$·$2H_2O$ (0.0.139 g, 0.0.166 mmol, 82%) as a bright orange solid, mp 193-197 °C dec (green liquid; open capillary). Anal. Calcd. for $C_{42}H_{48}Cl_3CoN_6$·$2H_2O$ (838.19): C 60.18, H 6.25, N 10.03; found C 60.23, H 6.24, N 9.90.

Data for product from **A**. NMR (3:1 v/v DMSO-d_6/CD_3OD, δ in ppm):[s8] ^1H (500 MHz) 7.54-7.49 (m, 0.17·12H, *o*-Ph), 7.48-7.43 (m, 0.83·12H, *o*-Ph), 7.34-7.22 (m, 0.17·18H and 0.83·18H, *m*-, *p*-Ph), 6.77 (br s, 0.17·6H, N**H**H'), 6.53 (d, $^3J_{HH}$ = 11 Hz, 0.83·6H, N**H**H'), 5.43 (br s, 0.83·6H, N**H**H'), 5.32 (br s, 0.17·6H, N**H**H'), 4.96 (s, 0.17·6H, C**H**NH_2), 4.77-4.62 (m, 0.83·6H, C**H**NH_2), 4.06 (br s, 20H, CD_3O**H**/**H**$_2O$);[s9] $^{13}C\{^1H\}$ (125 MHz) 137.6 (s, *i*-Ph), 129.2 (s, Ph),[s17] 129.0 (s, Ph), 128.9 (s, Ph), 128.6 (s, Ph), 63.7 (s, C**H**NH_2, 83%), 62.0 (s, C**H**NH_2, 17%).

Data for product from **B**. NMR (CD_3OD, δ in ppm):[s8] ^1H (500 MHz) 7.46-7.44 (m, 12H,

o), 7.30 (br s, 18H, *m*, *p*), 6.41 (d, 6H, $^3J_{HH}$ = 10 Hz, N**H**H'), 5.94 (bs s, 6H, NH**H'**), 4.88 (br s, 13H, CD_3O**H**/$\mathbf{H_2}O$),[s9] 4.58 (d, 6H, $^3J_{HH}$ = 10 Hz, C**H**NH_2); $^{13}C\{^1H\}$ (125 MHz): 137.3 (s, *i*-Ph), 130.2 (s, *p*-Ph), 130.0 and 129.1 (2 s, *o*-, *m*-Ph), 66.7 (s, C**H**NH_2).

Equilibration of diastereomers of (*S*,*S*)-3^{3+} 3X$^-$. A (Scheme 1, step D with Λ disastereomer).[s18] A 5 mm NMR tube was charged with Λ-(*S*,*S*)-**3**$^{3+}$ 3ClO_4^-·4H_2O (0.027 g, 0.025 mmol), activated charcoal (0.005 g), CD_3OD (0.5 mL), and a stir bar, and kept at 70 °C with stirring. The sample was monitored by $^{13}C\{^1H\}$ NMR (stir bar removed prior to each spectrum), which showed the isomerization of Λ-(*S*,*S*)-**3**$^{3+}$ 3ClO_4^- to Δ-(*S*,*S*)-**3**$^{3+}$ 3ClO_4^- (δ 63.6 ppm to 66.6 ppm), with a minor byproduct (δ 71.9 ppm) becoming increasingly visible after 24 h. Data (time, ratios): 4 h, 25/75/-, 22 h, 14/86/-, 68 h, 10/76/14, 150 h, 3/81/16). No other signals were evident. **B. (Scheme 1, step D with Δ disastereomer dominant).** A round bottom flask was charged with the 83:17 Δ/Λ mixture of (*S*,*S*)-**3**$^{3+}$ 3ClO_4^- (above; 0.118 g, 0.119 mmol), CH_3OH (10 mL), and activated charcoal (0.051 g), and fitted with a condenser. The mixture was heated at 70 °C. After 48 h, the mixture was filtered through Celite. The solvent was removed by rotary evaporation and dried by oil pump vacuum at room temperature to give Δ-(*S*,*S*)-**3**$^{3+}$ 3ClO_4^- (0.114 g, 0.115 mmol, 97%; triplicate runs gave 95% and 99%; <4% Λ)[s11b] as an orange solid, NMR data for which are given above. **C (Scheme 1, step F with diastereomer mixture).** A 5 mm NMR tube was charged with (*S*,*S*)-**3**$^{3+}$ 3Cl^- (0.030 g, 0.0373 mmol; 17:83 Λ/Δ), activated charcoal (0.0063 g), CD_3OD (0.5 mL), and a stir bar, and kept at 70 °C with stirring. The sample was monitored by $^{13}C\{^1H\}$ NMR (stir bar removed prior to each spectrum), which showed the gradual isomerization to a 61:39 Λ/Δ mixture (δ 66.6 ppm to 63.5 ppm). Data (time, ratios): 18 h, 58/42, 37 h, 61/39). No other signals were evident. **D (Scheme 1, step F with Δ diastereomer).** A 5 mm NMR tube was charged with Δ-(*S*,*S*)-**3**$^{3+}$ 3Cl^- (0.025 g, 0.0311 mmol), activated charcoal (0.0010 g), CD_3OD (0.5 mL), and a stir bar, and kept at 70 °C with stirring. The sample was monitored by $^{13}C\{^1H\}$ NMR (stir bar removed prior to each spectrum), which showed isomerization to a 57:43 Λ/Δ mixture (δ 66.6 ppm to 63.5 ppm). Data (time, ratios: 24 h, 54/46; 50 h, 57/43). No other signals were evident.

Λ-[Co((*S*,*S*)-dpen)$_3$]$^{3+}$ 2Cl$^-$BAr$_f^-$ (Λ-(*S*,*S*)-3^{3+} 2Cl$^-$BAr$_f^-$). A round bottom flask was charged with Λ-(*S*,*S*)-**3**$^{3+}$ 3Cl$^-$·3H$_2$O (0.320 g, 0.374 mmol), CH_2Cl_2 (15 mL) and Na$^+$ BAr$_f^-$ (0.382 g, 0.431 mmol). The sample was sonicated for 5 min, during which time the solvent became bright orange and a white precipitate (NaCl) formed. The mixture was filtered. The filtrate was loaded onto a silica gel column (1.9 × 15 cm), giving an orange band. The column was eluted with CH_2Cl_2/CH_3OH (100:0 to 98:2 v/v). The main orange band was collected. The solvent was removed by rotary evaporation and the residue dried by oil pump vacuum (room temperature, 14 h) to give Λ-(*S*,*S*)-**3**$^{3+}$ 2Cl$^-$BAr$_f^-$·2H$_2$O (0.5802 g, 0.3478 mmol, 93%) as an orange solid, mp 116-119 °C dec (open capillary). Anal. Calcd. for $C_{74}H_{60}BCl_2CoF_{24}N_6$·2H$_2$O (1665.95): C 53.35, H 3.87, N 5.04, Cl 4.26; found C 53.50, H 3.82, N 4.84, Cl 3.94.

NMR (CD_2Cl_2, δ in ppm): ^{1}H (500 MHz) BAr$_f^-$ at 7.73 (s, 8H, *o*), 7.54 (s, 4H, *p*); (*S*,*S*)-**2** ligand at 8.17 (br s, 6H, N**H**H'), 7.40-7.37 (m, 6H, *p*-Ph), 7.34-7.30 (m, 24H, *o*-, *m*-Ph), 4.48 (s, 6H, C**H**NH$_2$), 3.86 (br s, 6H, NH**H**'), 2.14 (br s, 7H, **H**$_2$O);[s9] ^{13}C{^{1}H} (125 MHz) BAr$_f^-$ at 162.3 (q, $^1J_{BC}$ = 49.4 Hz, *i*), 135.4 (s, *o*), 129.4 (q, $^2J_{CF}$ = 31.3 Hz, *m*), 125.2 (q, $^1J_{CF}$ = 271.0 Hz, **C**F$_3$), 118.1 (s, *p*); (*S*,*S*)-**2** ligand at 134.8 (s, *i*-Ph), 131.1 (s, *p*-Ph), 130.6 (s, *o*-Ph), 128.0 (s, *m*-Ph),[s16] 63.6 (s, **C**HNH$_2$). IR (powder film, cm^{-1}): 3039 (m, ν_{NH}), 1609 (m, δ_{NH}), 1354 (s, $\nu_{Ar\text{-}CF_3}$), 1275 (vs, ν_{CF}), 1119 (vs, δ_{CCN}); UV-visible (nm, 1.66 × 10^{-3} M in CH_2Cl_2 (ε, M^{-1} cm^{-1})): 455 (shoulder, 157). $[\alpha]_{18}^{589}$ = 0.0° (5.18 mg mL^{-1}, CH_2Cl_2); $[\alpha]_{18}^{546}$ = 23.1° (5.18 mg mL^{-1}, CH_2Cl_2).[s19]

Δ-[Co((*S*,*S*)-dpen)$_3$]$^{3+}$ 2Cl$^-$BAr$_f^-$ (Δ-(*S*,*S*)-3^{3+} 2Cl$^-$BAr$_f^-$). A round bottom flask was charged with a 83:17 mixture of Δ-/Λ-(*S*,*S*)-**3**$^{3+}$ 3Cl$^-$ (0.188 g, 0.234 mmol), CH_2Cl_2 (10 mL), Na$^+$ BAr$_f^-$ (0.240 g, 0.270 mmol), and CH_3OH (0.10 mL). The sample was sonicated for 5 min, during which time the solvent became bright orange as a small amount of a white solid (NaCl) precipitated. The mixture was filtered. The filtrate was loaded onto a silica gel column (1.9 × 14 cm), giving an orange band. The column was eluted with CH_2Cl_2/CH_3OH (100:0 to 97:3 v/v). Aliquots of the main orange band were collected. These were analyzed by TLC, and combined accordingly. The solvents were removed by rotary evaporation and the residues dried by oil pump

vacuum to give Λ-(*S*,*S*)-**3**$^{3+}$ 2Cl^{-}BAr$_f^{-}$·2H$_2$O (0.0586 g, 0.0352 mmol, 15%) and Δ-(*S*,*S*)-**3**$^{3+}$ 2Cl^{-}BAr$_f^{-}$·H$_2$O (0.2932 g, 0.1779 mmol, 76%).

Data for Δ-(*S*,*S*)-**3**$^{3+}$ 2Cl^{-}BAr$_f^{-}$·H$_2$O. When warmed (open capillary), the complex continually darkened and liquefied at 110 °C. Anal. Calcd. for $C_{74}H_{60}BCl_2CoF_{24}N_6 \cdot H_2O$ (1647.94): C 53.93, H 3.79, N 5.10, Cl 4.30; found C 53.96, H 4.02, N 4.98, Cl 4.20.

NMR (CD_2Cl_2/CH_3OH (0.40:0.001 mL, with the latter significantly enhancing solubility), δ in ppm): ^{1}H (500 MHz) BAr$_f^{-}$ at 7.73 (s, 8H, *o*), 7.55 (s, 4H, *p*); (*S*,*S*)-**2** ligand at 7.30-7.27 (m, 18H, *o*-, *p*-Ph), 7.22-7.19 (t, $^3J_{HH}$ = 7.5 Hz, 12H, *m*-Ph), 6.58 (br s, 6H, N**H**H'), 5.35 (br s, 6H, NH**H'**), 4.25 (s, 6H, C**H**NH$_2$), 2.53 (br s, 14H, CH_3O**H**/**H**$_2$O);[s9] ^{13}C{^{1}H} (125 MHz) BAr$_f^{-}$ at 162.3 (q, $^1J_{BC}$ = 49.6 Hz, *i*), 135.4 (s, *o*), 129.4 (q, $^2J_{CF}$ = 31.4 Hz, *m*), 125.2 (q, $^1J_{CF}$ = 271.0 Hz, **C**F$_3$), 118.0 (s, *p*); (*S*,*S*)-**2** ligand at 134.3 (s, *i*-Ph), 130.6 (s, *p*-Ph), 129.9 (s, *o*-Ph), 128.0 (s, *m*-Ph),[s16] 66.7 (s, **C**HNH$_2$). IR (powder film, cm^{-1}): 3068 (m, ν_{NH}), 1608 (m, δ_{NH}), 1574 (m, δ_{NH}), 1354 (s, $\nu_{Ar\text{-}CF_3}$), 1275 (vs, ν_{CF}), 1119 (vs, δ_{CCN}); UV-visible (nm, 1.66 × 10^{-3} M in CH_2Cl_2 (ε, M^{-1} cm^{-1})): 462 (191); $[\alpha]_{18}^{546}$ = –419.0° (5.25 mg mL^{-1}, CH_2Cl_2).

Λ-[Co((*S*,*S*)-dpen)$_3$]$^{3+}$ 3BAr$_f^{-}$ (Λ-(*S*,*S*)-3^{3+} 3BAr$_f^{-}$). **A**. A beaker was charged with Λ-(*S*,*S*)-**3**$^{3+}$ 2Cl^{-}BAr$_f^{-}$·2H$_2$O (0.170 g, 0.102 mmol), CH_2Cl_2 (15 mL), Na^{+} BAr$_f^{-}$ (0.188 g, 0.204 mmol, 2.00 equiv), and H$_2$O (15 mL). The biphasic mixture was vigorously stirred for 10 min and then allowed to stand. The lower orange CH_2Cl_2 phase was separated and allowed to evaporate in a hood to give Λ-(*S*,*S*)-**3**$^{3+}$ 3BAr$_f^{-}$·8H$_2$O as an orange solid (0.336 g, 0.0979 mmol, 96%). **B**. A beaker was charged with Λ-(*S*,*S*)-**3**$^{3+}$ 3Cl^{-}·3H$_2$O (0.170 g, 0.199 mmol), CH_2Cl_2 (15 mL), Na^{+} BAr$_f^{-}$ (0.532 g, 0.60 mmol, 3.0 equiv), and H$_2$O (15 mL). The biphasic mixture was vigorously stirred for 10 min, and then allowed to stand. The lower orange CH_2Cl_2 phase was separated and allowed to evaporate in a hood to give Λ-(*S*,*S*)-**3**$^{3+}$ 3BAr$_f^{-}$·8H$_2$O as an orange solid (0.644 g, 0.188 mmol, 94%), dec pt 68-98 °C (no melting), liquefies at 106 °C (open capillary). Anal. Calcd. for $C_{138}H_{84}B_3CoF_{72}N_6 \cdot 8H_2O$ (3429.55): C 48.33, H 2.94, N 2.45; found C 48.16, H 2.90, N 2.40.

NMR (acetone-d_6, δ in ppm):[s8] ^{1}H (500 MHz) BAr$_f^{-}$ at 7.79 (s, 24H, *o*), 7.67 (s, 12H, *p*);

(*S*,*S*)-**2** ligand at 7.40-7.37 (m, 6H, *p*-Ph), 7.34-7.30 (m, 24H, *o*-, *m*-Ph), 6.38 (br s, 6H, N**H**H'), 6.22 (br s, 6H, NH**H'**); 5.30 (s, 6H, C**H**NH_2), 2.95 (br s, 24H, $\mathbf{H}_2O$);[s9] $^{13}C\{^1H\}$ (125 MHz) BAr_f^- at 162.6 (q, $^1J_{BC}$ = 50.0 Hz, *i*), 135.5 (s, *o*), 130.0 (q, $^2J_{CF}$ = 32.5 Hz, *m*), 125.3 (q, $^1J_{CF}$ = 270.0 Hz, **C**F_3), 118.4 (m, *p*); (*S*,*S*)-**2** ligand at 135.5 (s, *i*-Ph), 130.8 (s, *p*-Ph), 130.3 (s, *o*-Ph), 129.4 (s, *m*-Ph),[s16] 64.1 (s, **C**HNH_2).

Δ-[Co((*S*,*S*)-dpen)$_3$]$^{3+}$ 3BAr$_f^-$ (Δ-(*S*,*S*)-3^{3+} 3BAr$_f^-$). A beaker was charged with Δ-(*S*,*S*)-**3**$^{3+}$ 2Cl$^-$BAr$_f^-$·H_2O (0.0824 g, 0.050 mmol), Na^+ BAr_f^- (0.0923 g, 0.100 mmol, 2.0 equiv), CH_2Cl_2 (10 mL), and H_2O (10 mL). The biphasic mixture was vigorously stirred for 10 min and then allowed to stand. The lower orange CH_2Cl_2 phase was separated and allowed to evaporate in the hood to give Δ-(*S*,*S*)-**3**$^{3+}$ 3BAr_f^-·9H_2O as an orange solid (0.158 g, 0.0458 mmol, 92%), which when warmed (open capillary) continually darkened and then liquefied at 90 °C. Anal. Calcd. for $C_{138}H_{84}B_3CoF_{72}N_6$·9$H_2O$ (3447.57): C 48.08, H 2.98, N 2.44; found C 48.04, H 2.78, N 2.46.

NMR (acetone-d_6, δ in ppm):[s8] ^1H (500 MHz) BAr_f^- at 7.80 (s, 24H, *o*), 7.67 (s, 12H, *p*); (*S*,*S*)-**2** ligand at 7.51-7.45 (m, 12H, *o*-Ph), 7.43-7.31 (m, 18H, *m*-, *p*-Ph), 6.87-6.70 (m, 6H, N**H**H'), 5.93 (br s, 6H, NH**H'**); 5.31-5.21 (m, 6H, C**H**NH_2), 3.01 (br s, 20H, $\mathbf{H}_2O$);[s9] $^{13}C\{^1H\}$ (125 MHz) BAr_f^- at 162.6 (q, $^1J_{BC}$ = 50.0 Hz, *i*), 135.5 (s, *o*), 130.0 (m, *m*), 125.3 (q, $^1J_{CF}$ = 270.0 Hz, **C**F_3), 118.4 (m, *p*); (*S*,*S*)-**2** ligand at 135.8 (s, *i*-Ph), 130.9 (s, *p*-Ph), 130.3 (s, *o*-Ph), 128.6 (s, *m*-Ph),[s16] 65.9 (s, **C**HNH_2).

Λ-[Co((*S*,*S*)-dpen)$_3$]$^{3+}$ 3BF$_4^-$ (Λ-(*S*,*S*)-3^{3+} 3BF$_4^-$). A round bottom flask was charged with a solution of Λ-(*S*,*S*)-**3**$^{3+}$ 3Cl^-·3H_2O (0.173 g, 0.202 mmol) in CH_3OH (15 mL) and Ag^+ BF_4^- (0.118 g, 0.606 mmol, 3.0 equiv). The mixture was sonicated for 10 min, and filtered through Celite. The solvent was removed from the filtrate by rotary evaporation. The residue was dried by oil pump vacuum (room temperature, 14 h) to give Λ-(*S*,*S*)-**3**$^{3+}$ 3BF_4^-·2H_2O as a bright orange solid (0.185 g, 0.187 mmol, 93%), mp 198-202 °C dec (open capillary). Anal. Calcd. for $C_{42}H_{48}B_3CoF_{12}N_6$·2$H_2O$ (992.24): C 50.84, H 5.28, N 8.47; found C 51.16, H 5.42, N 8.47.

^1H NMR (500 MHz, acetone-d_6, δ in ppm):[s8] 7.57-7.43 (m, 12H, *o*-Ph), 7.42-7.23 (m,

18H, *m-, p*-Ph), 5.83 (br s, 11H, N**H**H'),[s15] 5.18 (s, 6H, C**H**NH_2), 2.87 (s, 7H, $\mathbf{H_2}O$);[s9] ^{13}C {^1H} NMR (125 MHz, CD_3OD, δ in ppm):): 136.1 (s, *i*-Ph), 130.5 (s, *p*-Ph), 130.2, (s, *o*-Ph), 129.6 (s, *m*-Ph),[s16] 63.7 (s, **C**HNH_2).

Λ-[Co((*S*,*S*)-dpen)$_3$]$^{3+}$ 2BF$_4^-$BAr$_f^-$ (Λ-(*S*,*S*)-3^{3+} 2BF$_4^-$BAr$_f^-$). A round bottom flask was charged with a solution of Λ-(*S*,*S*)-**3**$^{3+}$ 2Cl$^-$BAr$_f^-$·2H_2O (0.9985 g, 0.599 mmol) in CH_2Cl_2 (4 mL), and Ag^+ BF_4^- (0.2412 g, 1.24 mmol, 2.07 equiv) was added with stirring. The heterogeneous mixture was sonicated for 10 min. The mixture was filtered through Celite. The solvent was removed from the filtrate by rotary evaporation. The residue was dried by oil pump vacuum (room temperature, 14 h) to give Λ-(*S*,*S*)-**3**$^{3+}$ 2BF$_4^-$BAr$_f^-$·3H_2O as a bright orange solid (1.019 g, 0.570 mmol, 95%), mp 140-147 °C dec (open capillary). Anal. Calcd. for $C_{74}H_{60}B_3CoF_{32}N_6$·3$H_2O$ (1786.67): C 49.75, H 3.72, N 4.70; found C 49.94, H 3.69, N 4.52.

NMR (CD_2Cl_2, δ in ppm): ^1H (500 MHz) BAr$_f^-$ at 7.73 (s, 8H, *o*), 7.56 (s, 4H, *p*); (*S*,*S*)-**2** ligand at 7.45 (t, $^1J_{HH}$ = 7.0 Hz, 6H, *p*-Ph), 7.40 (t, $^1J_{HH}$ = 7.0 Hz, 12H, *m*-Ph), 7.32 (d, $^1J_{HH}$ = 7.0 Hz, 12H, *o*-Ph), 6.04 (br s, 6H, N**H**H'), 4.52 (s, 6H, C**H**NH_2), 4.17 (br s, 6H, NH**H'**), 2.01 (s, 8H, $\mathbf{H_2}O$);[s9] $^{13}C\{^1H\}$ (125 MHz) BAr$_f^-$ at 162.2 (q, $^1J_{BC}$ = 48.8 Hz, *i*), 135.3 (s, *o*), 129.4 (q, $^2J_{CF}$ = 27.5 Hz, *m*), 125.1 (q, $^1J_{CF}$ = 271.3 Hz, **C**F_3), 118.1 (s, *p*); (*S*,*S*)-**2** ligand at 133.6 (s, *p*-Ph), 131.4 (s, *i*-Ph), 130.7, (s, *o*-Ph), 127.8 (s, *m*-Ph),[s16] 64.5 (s, **C**HNH_2). IR (powder film, cm^{-1}): 3254 (m, ν_{NH}), 1608 (m, δ_{NH}), 1354 (s, $\nu_{Ar\text{-}CF_3}$), 1277 (vs, ν_{CF}), 1121 (vs, δ_{CCN}); UV-visible (nm, 1.67 × 10^{-3} M in CH_2Cl_2 (ε, M^{-1} cm^{-1})): 451 (shoulder, 231); $[\alpha]_{18}^{546}$ = 50.6° (4.74 mg mL^{-1}, CH_2Cl_2).

Λ-[Co((*S*,*S*)-dpen)$_3$]$^{3+}$ 2PF$_6^-$BAr$_f^-$ (Λ-(*S*,*S*)-3^{3+} 2PF$_6^-$BAr$_f^-$). A round bottom flask was charged with a solution of Λ-(*S*,*S*)-**3**$^{3+}$ 2Cl$^-$BAr$_f^-$·2H_2O (0.1200 g, 0.072 mmol) in CH_2Cl_2 (2 mL). A solution of Ag^+ PF_6^- (0.0373 g, 0.148 mmol, 2.1 equiv) in CH_2Cl_2 (2 mL) was added with stirring. A white precipitate immediately formed. The mixture was sonicated (1 min) and filtered through Celite. The orange filtrate was washed with H_2O (2 × 1 mL) and the solvent was removed by rotary evaporation. The residue was dried by oil pump vacuum (room temperature, 5 h) to give Λ-(*S*,*S*)-**3**$^{3+}$ 2PF$_6^-$BAr$_f^-$·H_2O as a bright orange solid (0.1121 g, 0.060 mmol, 83%),

which when warmed (open capillary) continually darkened and then liquefied at 160 °C. Anal. Calcd. for $C_{74}H_{60}BCoF_{36}N_6P_2 \cdot H_2O$ (1866.96): C 47.61, H 3.35, N 4.50; found C 47.86, 3.49, 4.62.

NMR (CD_2Cl_2, δ in ppm): ^{1}H (500 MHz) BAr_f^- at 7.71 (s, 8H, *o*), 7.55 (s, 4H, *p*); (*S*,*S*)-**2** ligand at 7.47 (t, $^3J_{HH}$ = 7.0 Hz, 6H, *p*-Ph), 7.42 (t, $^3J_{HH}$ = 7.5 Hz, 12H, *m*-Ph), 7.29 (d, $^3J_{HH}$ = 7.0 Hz, 12H, *o*-Ph), 5.66 (br s, 6H, N**H**H'), 4.49 (s, 6H, C**H**NH_2), 4.37 (br s, 6H, NH**H'**), 1.85 (br s, 18H, $\mathbf{H}_2O$);[s9] $^{13}C\{^1H\}$ (125 MHz) BAr_f^- at 162.2 (q, $^1J_{BC}$ = 48.8 Hz, *i*), 135.3 (s, *o*), 129.4 (q, $^2J_{CF}$ = 33.8 Hz, *m*), 125.1 (q, $^1J_{CF}$ = 271.2 Hz, **C**F_3), 118.1 (s, *p*); (*S*,*S*)-**2** ligand at 133.0 (s, *i*-Ph), 131.9 (s, *p*-Ph), 131.0 (s, *o*-Ph), 127.8 (s, *m*-Ph),[s16] 64.0 (s, **C**HNH_2). IR (powder film, cm^{-1}): 3287 (m, ν_{NH}), 1609 (m, δ_{NH}), 1354 (s, $\nu_{Ar\text{-}CF_3}$), 1276 (vs, ν_{CF}), 1122 (vs, δ_{CCN}); UV-visible (nm, 1.67×10^{-3} M in CH_2Cl_2 (ε, M^{-1} cm^{-1})): 449 (shoulder, 302); $[\alpha]_{18}^{546}$ = 47.6° (4.42 mg mL^{-1}, CH_2Cl_2).

Representative ^{1}H NMR titration. A 5 mm NMR tube was charged with Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $2Cl^-BAr_f^- \cdot 2H_2O$ (0.0141 g, 0.00848 mmol) and CD_2Cl_2 (0.5 mL). A solution of **4a** (2.1 M in CD_2Cl_2) was added in increments of 0.001 mL (0.25 equiv) and ^{1}H NMR spectra were recorded. Selected peaks shifted, as shown by the spectra in Figure s3. Data (equiv of **4a**/ NH signals, δ in ppm): 0.25/4.010 and 8.127; 0.50/4.053 and 8.134; 0.75/4.094 and 8.141; 1.0/ 4.129 and 8.131; 1.25/4.165 and 8.155; 1.50/4.195 and 8.158; 1.75/4.204 and 8.162; 2.0/4.241 and 8.169; 2.50/4.28 and 8.179; 2.75/4.296 and 8.183; 3.0/4.31 and 8.178; 4.0/4.342 and 8.184; 5.0/4.368 and 8.196; 6.0/4.387 and 8.227; 7.0/4.405 and 8.236; 8.0/4.418 and 8.234; 9.0/4.432 and 8.249.

Syntheses of previously unreported nitroolefins. A (*trans*-2-acetoxy-β-nitrostyrene; 4h). A Schlenk flask was charged with *trans*-2-(2-nitrovinyl)phenol (0.5871 g, 3.54 mmol),[s1a] Et_3N (0.500 mL, 3.58 mmol, 1.01 equiv), and CH_2Cl_2 (10 mL, dried and degassed using a Glass Contour solvent purification system) under N_2. The solution was cooled to 0 °C and acetyl chloride (0.375 mL, 5.28 mmol, 1.49 equiv) was added dropwise by syringe with stirring. The cold bath was removed. After 12 h, CH_2Cl_2 (50 mL) was added. The mixture was washed with H_2O (50 mL), 1.0 M HCl, (50 mL), and brine (50 mL). The organic layer was dried (Na_2SO_4) and the

solvent was removed by rotary evaporation. The residue was chromatographed on a silica gel column (80:20 v/v hexanes/EtOAc). The solvent was removed from the combined product fractions by rotary evaporation. The residue was dried by oil pump vacuum at room temperature to give **4h** as a pale yellow solid (0.473 g, 2.28 mmol, 65%), which became a wax at 69-71 °C and liquefied at 74-76 °C (open capillary). Anal. Calcd. for $C_{10}H_9NO_4$ (207.18): C 57.97, H 4.38, N 6.76; found C 58.13, H 4.40, N 6.73. **B. (*trans*-2-benzoyloxy-β-nitrostyrene; 4i).** *trans*-2-(2-nitrovinyl)phenol (0.5943 g, 3.60 mmol),[s1a] Et_3N (0.630 mL, 4.52 mmol, 1.26 equiv), CH_2Cl_2 (10 mL, dried and degassed using a Glass Contour solvent purification system), and benzoyl chloride (0.790 mL, 6.81 mmol, 1.89 equiv) were combined in a procedure analogous to A. An identical workup gave **4i** as a pale yellow solid (0.6629 g, 2.46 mmol, 69%), which became a wax at 78-82 °C and liquefied at 87-89 °C (open capillary). Anal. Calcd. for $C_{15}H_{11}NO_4$ (269.25): C 66.91, H 4.12, N 5.20; found C 67.04, H 4.20, N 5.01.

Data for **4h**. NMR ($CDCl_3$, δ in ppm): ^{1}H (500 MHz) 8.06 (d, $^3J_{HH}$ = 13.5 Hz, 1H, C**H**-NO_2), 7.61-7.58 (m, 2H, C**H**=$CHNO_2$ and 1H of $C_6\mathbf{H}_4$), 7.52 (t, $^3J_{HH}$ = 8.5 Hz, 1H of $C_6\mathbf{H}_4$), 7.32 (t, $^3J_{HH}$ = 7.5 Hz, 1H of $C_6\mathbf{H}_4$), 7.23 (d, $^3J_{HH}$ = 8.5 Hz, 1H of $C_6\mathbf{H}_4$), 2.43 (s, 3H, C$\mathbf{H}_3$); ^{13}C{^{1}H} (125 MHz): 168.8 (s, **C**(O)Me), 150.2, 138.7, 133.2, 133.1, 129.1, 126.8, 123.8, 123.0 (8 × s, $\mathbf{C}_6H_4$, **C**H=**C**HNO_2), 21.2 (s, **C**H_3). IR (powder film, cm^{-1}): 3115 (w), 1753 (s), 1638 (m), 1510 (s), 1339 (vs), 1194 (vs), 963 (s), 758 (s).

Data for **4i**. NMR ($CDCl_3$, δ in ppm): ^{1}H (500 MHz) 8.24 (m, 2H, C**H**NO_2 and 1 H of $C_6\mathbf{H}_5$/$C_6\mathbf{H}_4$), 8.13 (d, $^3J_{HH}$ = 13.5 Hz, 1H, C**H**=$CHNO_2$), 7.70 (t, $^3J_{HH}$ = 7.5 Hz, 1H of $C_6\mathbf{H}_5$/ $C_6\mathbf{H}_4$), 7.66-7.56 (m, 5H of $C_6\mathbf{H}_5$/$C_6\mathbf{H}_4$), 7.38-7.33 (m, 2H of $C_6\mathbf{H}_5$/$C_6\mathbf{H}_4$); ^{13}C{^{1}H} (125 MHz) 164.7 (s, **C**(O)Ph), 150.6 138.7, 134.5, 133.2, 133.2, 130.5, 129.2, 129.1, 128.5, 126.9, 124.0, 123.4 (12 × s, **C**H=**C**HNO_2, $\mathbf{C}_6H_4$, $\mathbf{C}_6H_5$). IR (powder film, cm^{-1}): 3105 (w), 1742 (s), 1340 (s), 1209 (vs), 1057 (vs), 700 (vs).

Rate profiles, Figure 2. A 5 mm NMR tube was charged with a solution of **4d** (0.0180 g, 0.101 mmol), dimethyl malonate (**5c**, 0.0127 mL, 0.111 mmol, 1.10 equiv), catalyst (0.0020 mmol, 0.020 equiv), and Ph_2SiMe_2 (0.0020 mL, internal standard) in CD_2Cl_2 (1.0 mL). A ^{1}H

NMR spectrum was recorded to measure the initial ratio of **4d** to the standard. Then Et_3N (0.0050 mL, 0.036 mmol, 0.36 equiv) was added and the conversion to **6ac** was periodically measured by ^1H NMR. After 2 h, the mixture was loaded directly onto a plug of silica gel. The **6ac** was eluted with hexanes/EtOAc (1:1 v/v, 50 mL). The solvent was removed by rotary evaporation. The ee was assayed by chiral HPLC.[s20]

Reactions, Scheme 3. A (entries 1-6). A 5 mm NMR tube was charged with a solution of **4a** (0.0054 g, 0.036 mmol, 1.0 equiv), dialkyl malonate (**5**, 0.039 mmol, 1.1 equiv), catalyst (0.0036 mmol, 0.10 equiv), and Ph_2SiMe_2 (0.0020 mL, internal standard) in CD_2Cl_2 (0.40 mL). A ^1H NMR spectrum was recorded to measure the initial ratio of the nitroolefin to the standard. Then Et_3N (0.0050 mL, 0.0036 g, 0.036 mmol, 1.0 equiv) was added. The conversion was monitored by ^1H NMR. After the specified time (Scheme 3), the mixture was loaded onto a plug of silica gel. The organic product (**6aa-ac**) was eluted with hexanes/EtOAc (1:1 v/v, 50 mL). The solvent was removed by rotary evaporation. The product ee was assayed by chiral HPLC.[s20] **B (entries 7-11).** A 5 mm NMR tube was charged with a solution of **4a** (0.0149 g, 0.010 mmol, 1.0 equiv), **5c**, (0.0138 mL, 0.0158 g, 0.120 mmol, 1.2 equiv), catalyst (0.010 mmol, 0.10 equiv), and Ph_2SiMe_2 (0.0020 mL, internal standard) in acetone-d_6 (0.7 mL). A ^1H NMR spectrum was recorded to measure the initial ratio of the nitroolefin to the standard. The sample was cooled to 0 °C, and Et_3N (0.0140 mL, 0.0101 g, 0.10 mmol, 1.0 equiv) was added. The conversion to **6ac** was monitored by ^1H NMR. After the specified time (Scheme 3), the mixture was loaded directly onto a plug of silica gel. The **6ac** was eluted with hexanes/EtOAc (7:3 v/v, 50 mL). The solvent was removed by rotary evaporation. The ee was assayed by chiral HPLC.[s20]

Reactions, Scheme 4. A (with Λ-(*S*,*S*)-3^{3+} $2Cl^-BAr_f^-$). A 5 mm NMR tube was charged with a solution of nitroolefin (0.036 mmol, 1.0 equiv), Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $2Cl^-BAr_f^-\cdot 2H_2O$ (0.0059 g, 0.0036 mmol, 0.10 equiv), **5c** (0.0045 mL, 0.0052 g, 0.039 mmol, 1.1 equiv), and Ph_2SiMe_2 (0.0020 mL, internal standard) in acetone-d_6 (0.40 mL). A ^1H NMR spectrum was recorded to measure the initial ratio of the nitroolefin to the standard. The sample was cooled to 0 °C, and Et_3N (0.0050 mL, 0.0036 g, 0.036 mmol, 1.0 equiv) was added. The conversion was monitored

by ^{1}H NMR. After the specified time (Scheme 4), the mixture loaded onto a plug of silica gel. The organic product (**6ac-jc**) was eluted with hexanes/EtOAc (1:1 v/v). The solvent was removed by rotary evaporation. The product was dried by oil pump vacuum at room temperature and the ee assayed by chiral HPLC (Figures s4-s17).[s20] **B (with Λ-(*S*,*S*)-3^{3+} 2BF$_4^-$BAr$_f^-$).** A round bottom flask was charged with a solution of nitroolefin (0.355 mmol, 1.0 equiv), Λ-(*S*,*S*)-**3**$^{3+}$ 2BF$_4^-$BAr$_f^-$·3H$_2$O (0.0634 g, 0.0355 mmol, 0.10 equiv), and **5c** (0.0458 mL, 0.0529 g, 1.13 equiv) in acetone (3.3 mL), and cooled to 0 °C. Then Et$_3$N (0.0495 mL, 0.0359 g, 0.355 mmol, 1.0 equiv) was added. The reaction was monitored by TLC. After the specified time (Scheme 4), the solvent was removed by rotary evaporation and the residue was dissolved in CH_2Cl_2 (2 mL). The orange solution was chromatographed on a silica gel column (1.9 × 14 cm, 9:1 v/v hexanes/EtOAc). The solvent was removed from the product containing fractions by rotary evaporation. The product was dried by oil pump vacuum at room temperature (yields: Scheme 4) and the ee assayed by chiral HPLC (Figures s4-s17).[s20] **C (with Λ-(*S*,*S*)-3^{3+} 3BF$_4^-$).** A 5 mL vial was charged with a solution of nitroolefin (0.10 mmol, 1.0 equiv), Λ-(*S*,*S*)-**3**$^{3+}$ 3BF$_4^-$·2H$_2$O (0.0099 g, 0.010 mmol, 0.1 equiv), **5c** (0.0138 mL, 0.0158 g, 0.120 mmol, 1.2 equiv), and Ph_2SiMe_2 (0.0020 mL, internal standard) in acetone-d_6 (0.70 mL). A ^{1}H NMR spectrum was recorded to measure the initial ratio of the nitroolefin to the standard. The sample was cooled to 0 °C, and Et$_3$N (0.0140 mL, 0.0101 g, 0.10 mmol, 1.0 equiv) was added. The reaction was monitored by ^{1}H NMR and TLC. After the specified time (Scheme 4), the mixture was worked up as described in B.

Reactions, Scheme 5. A 1.5 mL vial was charged with a solution of azodicarboxylate **7** (0.023 g, 0.10 mmol), catalyst (0.0050 mmol, 0.05 equiv), and β-keto ester **8** (0.11 mmol, 1.10 equiv) in CH_2Cl_2 (1.0 mL). Then N-methylmorpholine (0.011 mL, 0.10 mmol, 1.0 equiv) was added. The reaction was monitored by TLC. After the specified time (Scheme 5), the mixture loaded onto a plug of silica gel. The organic product (**9**) was eluted with hexanes/EtOAc (9:1 v/v). The solvent was removed by rotary evaporation. The product was dried by oil pump vacuum at room temperature and the ee assayed by chiral HPLC (Figures s18-s19).[s26]

Catalyst recycling, Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ 2Cl$^-$BAr$_f^-$. A round bottom flask was charged with a solution of **4a** (0.0529 g, 0.355 mmol, 1.0 equiv), Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ 2Cl$^-$BAr$_f^-$·2H$_2$O (0.0543 g, 0.0326 mmol, 0.0918 equiv), and **5c** (0.0460 mL, 0.401 mmol, 1.13 equiv) in acetone (3.3 mL), and cooled to 0 °C. Then Et$_3$N (0.0460 mL, 0.0333 g, 0.330 mmol, 0.93 equiv) was added. The reaction was monitored by TLC. After 15 h, the solvent was removed by rotary evaporation and the residue was dissolved in CH$_2$Cl$_2$ (2 mL). The orange solution was washed with 3.0 M HCl (1 mL) and H$_2$O (2 × 1 mL) and chromatographed on a silica gel column (1.9 × 14 cm, 9:1 v/v hexanes/EtOAc). The solvent was removed from the organic product containing fractions by rotary evaporation and oil pump vacuum to give **6ac** as a white solid (0.0940 g, 0.334 mmol, 94%), which was analyzed by HPLC and ^{1}H and ^{13}C{^{1}H} NMR as described below. The column was then washed with CH$_2$Cl$_2$ and the orange catalyst band was eluted with CH$_2$Cl$_2$/CH$_3$OH (98:2 v/v). The solvent was removed by rotary evaporation and oil pump vacuum at room temperature to recover Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ 2Cl$^-$BAr$_f^-$·H$_2$O (0.0526 g, 0.0319 mmol, 98%). Anal. Calcd. for C$_{74}$H$_{60}$BCl$_2$CoF$_{24}$N$_6$·H$_2$O (1647.94): C 53.91, H 3.79, N 5.10; found C 53.84, H 4.08, N 4.96.

Diisopropyl 2-(2-nitro-1-phenylethyl)malonate (6aa).[s21] This known compound was obtained as a spectroscopically pure colorless oil per the general procedures for Scheme 3. NMR (CDCl$_3$, δ in ppm):[s22] ^{1}H (500 MHz) 7.32-7.22 (m, 5H, C$_6$**H**$_5$), 5.08 (sept, $^3J_{HH}$ = 6.0 Hz, 1H, C**H**(CH$_3$)$_2$), 4.92 (dd, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 4.5 Hz, 1H, C**H**H'NO$_2$), 4.86-4.60 (m, 2H, C'**H**-(C'H$_3$)$_2$ and CH**H**'NO$_2$), 4.20 (td, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, C**H**=CH$_2$NO$_2$), 3.75 (d, $^3J_{HH}$ = 9.5 Hz, 1H, C**H**(CO$_2$*i*Pr)$_2$), 1.24 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH(C**H**$_3$)$_2$), 1.07 (d, $^3J_{HH}$ = 6.0 Hz, 3H, C'H((C**H**$_3$)(C'H$_3$))), 1.01 (d, $^3J_{HH}$ = 6.5 Hz, 3H, C'H((CH$_3$)(C'**H**$_3$))); ^{13}C{^{1}H} (125 MHz): 167.2 (s, **C**O$_2$*i*Pr), 166.5 (s, **C**'O$_2$*i*Pr), 136.4 (s, *i*), 129.0 (s, *o*), 128.4 (s, *p*), 128.3 (s, *m*),[s16] 78.1 (s, **C**H$_2$NO$_2$), 70.1 (s, **C**H(CH$_3$)$_2$), 69.7 (s, **C**'H(C'H$_3$)$_2$), 55.3 (s, **C**H(CO$_2$*i*Pr)$_2$), 43.1 (s, **C**H=CH$_2$NO$_2$), 21.7, 21.6, 21.41, 21.39 (4 × s, 4 × **C**H$_3$).

Enantiomeric excesses were determined by HPLC (see Figure s4) with a Chiralcel OD column (95:05 v/v hexane/isopropanol, 0.75 mL/min, λ = 220 nm); for Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ 2Cl$^-$BAr$_f^-$, t_R = 10.8 min (major), 13.3 min (minor); for Δ-(*S*,*S*)-$\mathbf{3}^{3+}$ 2Cl$^-$BAr$_f^-$, similar but with major/min-

or reversed.[s20]

Diethyl 2-(2-nitro-1-phenylethyl)malonate (6ab).[s21] This known compound was obtained as a spectroscopically pure colorless oil per the general procedures for Scheme 3. NMR ($CDCl_3$, δ in ppm):[s22] ^1H (500 MHz) 7.33-7.22 (m, 5H, $C_6\mathbf{H}_5$), 4.92 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, C**H**H'NO_2), 4.86 (dd, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 9.0 Hz, 1H, CH**H**'NO_2), 4.26-4.19 (m, 3H, C**H**$_2$$CH_3$ and C**H**=CH_2NO_2), 4.00 (q, $^3J_{HH}$ = 7.5 Hz, 2H, C'**H**$_2$C'H_3), 3.81 (d, $^3J_{HH}$ = 9.5 Hz, 1H, C**H**$(CO_2Et)_2$), 1.26 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_2C**H**$_3$), 1.04 (t, $^3J_{HH}$ = 7.0 Hz, 3H, C'H_2C'**H**$_3$); $^{13}C\{^1H\}$ (125 MHz): 167.6 (s, **C**O_2Et), 166.9 (s, **C**'O_2Et), 136.3 (s, *i*), 129.1 (s, o), 128.5 (s, *p*) 128.1 (s, *m*),[s16] 77.8 (s, **C**H_2NO_2), 62.3 (s, **C**H_2CH_3), 62.0 (s, **C**'H_2C'H_3), 55.1 (s, **C**H$(CO_2Et)_2$), 43.1 (s, **C**H=CH_2NO_2), 14.1 (s, **C**H_3), 13.9 (s, **C**'H_3).

Enantiomeric excesses were determined by HPLC (see Figure s5) with a Chiralpak AS-H column (90:10 v/v hexane/isopropanol, 1.0 mL/min, λ = 220 nm); for Λ-(*S*,*S*)-**3**$^{3+}$ 2$Cl^-BAr_f^-$, t_R = 12.7 min (minor), 14.3 min (major); for Δ-(*S*,*S*)-**3**$^{3+}$ 2$Cl^-BAr_f^-$, similar but with major/minor reversed.[s20]

Dimethyl 2-(2-nitro-1-phenylethyl)malonate (6ac).[s21] This known compound was isolated as a white solid per the general procedures for Scheme 4. NMR ($CDCl_3$, δ in ppm):[s22] ^1H (500 MHz) 7.33-7.21 (m, 5H, $C_6\mathbf{H}_5$), 4.93 (dd, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, C**H**H'NO_2), 4.87 (dd, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 9.0 Hz, 1H, CH**H**'NO_2), 4.24 (td, $^3J_{HH}$ = 9.0 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, C**H**=CH_2NO_2), 3.86 (d, $^3J_{HH}$ = 9.0 Hz, 1H, C**H**$(CO_2Me)_2$), 3.75 (s, 3H, C**H**$_3$), 3.54 (s, 3H, C'**H**$_3$); $^{13}C\{^1H\}$ (125 MHz) 167.9 (s, **C**O_2Me), 167.3 (s, **C**'O_2Me), 136.2 (s, *i*), 129.1 (s, *o*) 128.4 (s, *p*), 128.0 (s, *m*), 77.5 (s, **C**H_2NO_2), 54.8 (s, **C**H$(CO_2Me)_2$), 53.1 (s, **C**H_3), 52.9 (s, **C**'H_3), 43.0 (s, **C**H=CH_2NO_2).

Enantiomeric excesses were determined by HPLC (see Figure s6) with a Chiralpak AD column (98:02 v/v hexane/isopropanol, 1.0 mL/min, λ = 220 nm); for Λ-(*S*,*S*)-**3**$^{3+}$ 2$BF_4^-BAr_f^-$ (Λ-(*S*,*S*)-**3**$^{3+}$ 2$Cl^-BAr_f^-$ similar), t_R = 32.4 min (major), 42.3 min (minor); for Λ-(*S*,*S*)-**3**$^{3+}$ 3BF_4^-, t_R = 33.3 min (major), 43.4 min (minor); for Δ-(*S*,*S*)-**3**$^{3+}$ 2$Cl^-BAr_f^-$, similar but with major/minor reversed.[s20]

Dimethyl 2-(2-nitro-1-α-naphthylethyl)malonate (6bc).[s23a] This known compound was isolated as a colorless oil per the general procedures for Scheme 4. NMR ($CDCl_3$, δ in ppm):[s22] ^{1}H (500 MHz) 8.18 (d, $^3J_{HH}$ = 8.5 Hz, 1H of $C_{10}\mathbf{H}_7$), 7.87 (d, $^3J_{HH}$ = 8.0 Hz, 1H of $C_{10}\mathbf{H}_7$), 7.80 (d, $^3J_{HH}$ = 8.0 Hz, 1H of $C_{10}\mathbf{H}_7$), 7.62 (t, $^3J_{HH}$ = 8.5 Hz, 1H of $C_{10}\mathbf{H}_7$), 7.53 (t, $^3J_{HH}$ = 8.0 Hz, 1H of $C_{10}\mathbf{H}_7$), 7.44-7.38 (m, 2H of $C_{10}\mathbf{H}_7$), 5.25-5.16 (m, 2H, C**H**H′NO_2 and C**H**=CH_2NO_2), 5.07 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 4.5 Hz, 1H, CH**H**′NO_2), 4.12 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C**H**$(CO_2Me)_2$), 3.72 (s, C**H**$_3$), 3.54 (s, C′**H**$_3$); $^{13}C\{^1H\}$ (125 MHz) 168.1 (s, **C**O_2Me), 167.6 (s, **C**′O_2Me), 134.3, 132.3, 131.1, 129.4, 129.2, 127.2, 126.2, 125.2, 124.1, 122.3 (10 × s, **C**$_{10}H_7$), 76.7 (s, **C**H_2NO_2), 54.6 (s, **C**H$(CO_2Me)_2$), 53.1 (s, **C**H_3), 53.0 (s, **C**′H_3), 36.9 (s, **C**H=CH_2NO_2).

Enantiomeric excesses were determined by HPLC (see Figure s7) with a Chiralpak AD column (90:10 v/v hexane/isopropanol, 1.0 mL/min, λ = 254 nm); for all catalysts t_R = 13.5-14.1 min (major), 18.9-19.6 min (minor).[s20]

Dimethyl 2-(2-nitro-1-β-naphthylethyl)malonate (6cc).[s23b] This known compound was isolated as a yellow solid per the general procedures for Scheme 4. NMR ($CDCl_3$, δ in ppm):[s22] ^{1}H (500 MHz) 7.83-7.79 (m, 3H of $C_{10}\mathbf{H}_7$), 7.70 (s, 1H of $C_{10}\mathbf{H}_7$), 7.50-7.48 (m, 2H of $C_{10}\mathbf{H}_7$), 7.34 (d, $^3J_{HH}$ = 8.5 Hz, 1H of $C_{10}\mathbf{H}_7$), 5.01 (d, $^3J_{HH}$ = 8.0 Hz, 2H, C**H**$_2NO_2$), 4.43 (q, $^3J_{HH}$ = 7.0 Hz, 1H, C**H**=CH_2NO_2), 3.98 (d, $^3J_{HH}$ = 9.0 Hz, 1H, C**H**$(CO_2Me)_2$), 3.77 (s, 3H, C**H**$_3$), 3.54 (s, 3H, C′**H**$_3$); $^{13}C\{^1H\}$ (125 MHz) 166.0 (s, **C**O_2Me), 167.4 (s, **C**′O_2Me), 133.7, 133.4, 133.2, 129.1, 128.1, 127.8, 127.5, 126.7, 126.6, 125.3 (10 × s, **C**$_{10}H_7$), 77.5 (s, **C**H_2NO_2), 54.9 (s, **C**H-$(CO_2Me)_2$), 53.2 (s, **C**H_3), 53.0 (s, **C**′H_3), 43.2 (**C**H=CH_2NO_2).

Enantiomeric excesses were determined by HPLC (see Figure s8) with a Chiralcel OD column (70:30 v/v hexane/isopropanol, 1.0 mL/min, λ = 254 nm); for Λ-(*S*,*S*)-**3**$^{3+}$ 2$BF_4^-$$BAr_f^-$, t_R = 14.4 min (major), 39.2 min (minor); for Λ-(*S*,*S*)-**3**$^{3+}$ 3BF_4^- (older column), t_R = 12.5 min (major), 37.0 min (minor).[s20]

Dimethyl 2-(2-nitro-1-(4-methoxyphenyl)ethyl)malonate (6dc).[s23a,b] This known compound was isolated as a colorless oil per the general procedures for Scheme 4. NMR ($CDCl_3$, δ

in ppm):[s22] ^{1}H (500 MHz) 7.14 (d, $^3J_{HH}$ = 8.5 Hz, 2H, *m* to CH), 6.83 (d, $^3J_{HH}$ = 8.5 Hz, 2H, *o* to CH), 4.89 (dd, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, C**H**H'NO_2), 4.82 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 9.5 Hz, 1H, CH**H**'NO_2), 4.19 (td, $^3J_{HH}$ = 9.0 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, C**H**=CH_2NO_2), 3.82 (d, $^3J_{HH}$ = 9.5 Hz, 1H, C**H**$(CO_2Me)_2$), 3.77 (s, 3H, $CO_2C\mathbf{H}_3$), 3.76 (s, 3H, C'O_2C'$\mathbf{H}_3$), 3.57 (s, 3H, ArOC$\mathbf{H}_3$); $^{13}C\{^1H\}$[s24] (125 MHz) 168.0 (s, **C**O_2Me), 167.4 (s, **C**'O_2Me), 159.6 (s, *p* to CH), 129.1 (s, *o* to CH), 128.0 (s, *i* to CH), 114.5 (s, *m* to CH), 77.8 (s, **C**H_2NO_2), 55.3 (s, ArO-**C**H_3), 55.0 (**C**H$(CO_2Me)_2$), 53.1 (s, $CO_2\mathbf{C}H_3$), 53.0 (s, C'O_2**C**'H_3), 42.4 (s, **C**H=CH_2NO_2).

Enantiomeric excesses were determined by HPLC (see Figure s9) with a Chiralpak AD column (80:20 v/v hexane/isopropanol, 1.0 mL/min, λ = 220 nm); for all catalysts t_R = 11.5-11.7 min (major), 17.5-18.2 min (minor).[s20]

Dimethyl 2-(2-nitro-1-(3,4-dichlorophenyl)ethyl)malonate (6ec). This new compound was isolated as a white solid per the general procedures for Scheme 4. NMR ($CDCl_3$, δ in ppm):[s22] ^{1}H (500 MHz) 7.40 (d, $^3J_{HH}$ = 9.0 Hz, 1H of $C_6\mathbf{H}_3$), 7.35 (s, 1H of $C_6\mathbf{H}_3$), 7.10 (d, $^3J_{HH}$ = 8.5 Hz, 1H of $C_6\mathbf{H}_3$), 4.90 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, C**H**H'NO_2), 4.85 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 9.5 Hz, 1H, CH**H**'NO_2), 4.20 (td, $^3J_{HH}$ = 9.0 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, C**H**=CH_2NO_2), 3.82 (d, $^3J_{HH}$ = 9.5 Hz, 1H, C**H**$(CO_2Me)_2$), 3.77 (s, 3H, C$\mathbf{H}_3$), 3.62 (s, 3H, C'$\mathbf{H}_3$); $^{13}C\{^1H\}$ (125 MHz) 167.5 (s, **C**O_2Me), 167.0 (s, **C**'O_2Me), 136.5, 133.3, 132.9, 131.1, 130.2, 127.4 (6 × s, $\mathbf{C}_6H_3$), 76.9 (s, **C**H_2NO_2), 54.4 (s, **C**H$(CO_2Me)_2$) , 53.3 (**C**H_3), 53.2 (**C**'H_3), 42.1 (**C**H=CH_2NO_2). IR (powder film, cm^{-1}): 1744 (s), 1715 (s), 1549 (vs), 1265 (s), 1611 (s). mp 78-81 °C (open capillary). Anal. Calcd. for $C_{13}H_{13}Cl_2NO_6$ (350.15): C 44.59, H 3.74, N 4.00; found C 44.82, H 3.82, N 4.02.

Enantiomeric excesses were determined by HPLC (see Figure s10) with a Chiralpak AS-H column (90:10 v/v hexane/isopropanol, 1.0 mL/min, λ = 220 nm); for all catalysts t_R = 20.4-21.3 min (minor), 22.7-23.5 min (major).[s20]

Dimethyl 2-(2-nitro-1-(pyridine-3-yl)ethyl)malonate (6fc).[s23a] This known compound was isolated as an off white solid per the general procedures for Scheme 4. NMR ($CDCl_3$, δ in ppm):[s22] ^{1}H (500 MHz) 8.55-8.52 (m, 2H of $C_5\mathbf{H}_4$N), 7.59 (dt, $^3J_{HH}$ = 8.0 Hz, J_{HH} = 2.0 Hz, 1H

of $C_5\mathbf{H}_4N$), 7.27-7.25 (m, 1H of $C_5\mathbf{H}_4N$), 4.94 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 8.5 Hz, C**H**H'NO_2), 4.89 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 9.5 Hz, 1H, CH**H**'NO_2), 4.26 (td, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 5.0 Hz, C**H**=CH_2NO_2), 3.86 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C**H**$(CO_2Me)_2$), 3.76 (s, C**H**$_3$), 3.58 (s, C'**H**$_3$); $^{13}C\{^1H\}$ (125 MHz) 167.6 (s, **C**O_2Me), 167.0 (s, **C**'O_2Me), 149.9, 149.7, 135.5, 132.1, 123.8 (5 × s, **C**$_5H_4N$), 76.9 (s, **C**H_2NO_2), 54.3 (s, **C**H$(CO_2Me)_2$), 53.3 (s, **C**H_3), 53.2 (s, **C**'H_3), 40.7 (s, **C**H=CH_2NO_2).

Enantiomeric excesses were determined by HPLC (see Figure s11) with a Chiralpak AD column (60:40 v/v hexane/isopropanol, 1.0 mL/min, λ = 220 nm); for Λ-(*S*,*S*)-**3**$^{3+}$ $2BF_4^-BAr_f^-$ (Λ-(*S*,*S*)-**3**$^{3+}$ $2Cl^-BAr_f^-$ similar), t_R = 6.8 min (major), 9.2 min (minor).[s20]

Dimethyl 2-(2-nitro-1-(2-trifluoromethylphenyl)ethyl)malonate (6gc). This new compound was isolated as a white solid per the general procedures for Scheme 4. NMR ($CDCl_3$, δ in ppm):[s22] ^1H (500 MHz) 7.72 (d, $^3J_{HH}$ = 7.5 Hz, 1H of $C_6\mathbf{H}_4$), 7.53 (t, $^3J_{HH}$ = 7.5 Hz, 1H of $C_6\mathbf{H}_4$), 7.43 (t, $^3J_{HH}$ = 8.0 Hz, 1H of $C_6\mathbf{H}_4$), 7.37 (d, $^3J_{HH}$ = 8.0 Hz, 1H of $C_6\mathbf{H}_4$), 5.16 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 7.5 Hz, 1H, C**H**H'NO_2), 4.94 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 4.5 Hz, 1H, CH**H**'NO_2), 4.65 (td, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 4.5 Hz, 1H, C**H**=CH_2NO_2), 4.11 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C**H**$(CO_2Me)_2$), 3.75 (s, 3H, C**H**$_3$), 3.64 (s, 3H, C'**H**$_3$); ^{13}C (125 MHz) 168.0 (s, **C**O_2Me), 167.3 (s, **C**'O_2Me), 135.1, 132.5 (2 × s, **C**$_6H_4$), 129.0 (q, $^2J_{CF}$ = 29.8 Hz, **C**CF_3), 128.6, 128.0 (2 × s, **C**$_6H_4$), 127.3 (q, $^3J_{CF}$ = 5.9 Hz, **C**H**C**CF_3), 124.2 (q, $^1J_{CF}$ = 272.6 Hz, **C**F_3), 76.6 (s, **C**H_2NO_2), 54.0 (s, **C**H$(CO_2Me)_2$), 53.2 (**C**H_3), 53.1 (**C**'H_3), 38.1 (s, **C**H=CH_2NO_2). IR (powder film, cm^{-1}): 2957 (w), 1751 (s), 1734 (s), 1549 (s), 1126 (vs), 777 (s). mp 76-79 °C (open capillary). Anal. Calcd. for $C_{14}H_{14}F_3NO_6$ (349.26): C 48.14, H 4.04, N 4.01; found C 47.91, H 3.93, N 3.91.

Enantiomeric excesses were determined by HPLC (see Figure s12) with a Chiralcel OD column (95:05 v/v hexane/isopropanol, 1.0 mL/min, λ = 220 nm); for all catalysts t_R = 12.7 min (minor), 26.6-28.6 min (major).[s20]

Dimethyl 2-(2-nitro-1-(2-acetoxyphenyl)ethyl)malonate (6hc). This new compound was isolated as a colorless oil per the general procedures for Scheme 4. NMR ($CDCl_3$, δ in

ppm):[s22] ^{1}H (500 MHz) 7.32 (t, $^3J_{HH}$ = 7.0 Hz, 1H of $C_6\mathbf{H}_4$), 7.27-7.25 (m, 1H of $C_6\mathbf{H}_4$), 7.20 (t, $^3J_{HH}$ = 7.5 Hz, 1H of $C_6\mathbf{H}_4$), 7.15 (d, $^3J_{HH}$ = 8.0 Hz, 1H of $C_6\mathbf{H}_4$), 4.94-4.86 (m, 2H, $C\mathbf{H}_2$-NO_2), 4.50 (q, $^3J_{HH}$ = 7.0 Hz, 1H, $C\mathbf{H}$=CH_2NO_2), 3.92 (d, $^3J_{HH}$ = 8.5 Hz, 1H, $C\mathbf{H}(CO_2Me)_2$), 3.74 (s, 3H, $OC\mathbf{H}_3$), 3.59 (s, 3H, $OC'\mathbf{H}_3$), 2.39 (s, 3H, $C\mathbf{H}_3$); $^{13}C\{^1H\}$ (125 MHz) 169.2, 168.0, 167.4 (3 × s, $\mathbf{C}O_2Me$, $\mathbf{C}'O_2Me$, $\mathbf{C}(O)Me$), 148.7, 129.4, 128.5, 128.2, 126.5, 123.5 (6 × s, $\mathbf{C}_6H_4$), 76.7 (s, $\mathbf{C}H_2NO_2$), 53.8 (s, $\mathbf{C}H(CO_2Me)_2$), 53.1 (s, $O\mathbf{C}H_3$, $OC'H_3$), 36.7 (s, $\mathbf{C}H$=CH_2NO_2), 21.2 (s, $\mathbf{C}H_3$), IR (neat oil, cm^{-1}): 2957 (w), 1734 (vs), 1555 (s), 1192 (s), 1171 (s). Anal. Calcd. for $C_{15}H_{17}NO_8$ (339.30): C 53.10, H 5.05, N 4.13; found C 53.39, H 5.11, N 4.11.

Enantiomeric excesses were determined by HPLC (see Figure s13) with a Chiralcel OD column (90:10 v/v hexane/isopropanol, 1.0 mL/min, λ = 220 nm); for Λ-(*S*,*S*)-**3**$^{3+}$ 2$BF_4^-$$BAr_f^-$ (Λ-(*S*,*S*)-**3**$^{3+}$ 2$Cl^-$$BAr_f^-$ similar), t_R = 18.9 min (minor), 28.5 min (major)); for Λ-(*S*,*S*)-**3**$^{3+}$ 3BF_4^- (older column), t_R = 19.7 min (minor), 31.3 min (major).[s20]

Dimethyl 2-(2-nitro-1-(2-benzoyloxyphenyl)ethyl)malonate (6ic). This new compound was isolated as a pale yellow oil per the general procedures for Scheme 4. NMR ($CDCl_3$, δ in ppm):[s22] ^{1}H (500 MHz) 8.27 (d, $^3J_{HH}$ = 7.0 Hz, 2H of $C_6\mathbf{H}_5$/$C_6\mathbf{H}_4$), 7.69 (t, $^3J_{HH}$ = 7.0 Hz, 1H of $C_6\mathbf{H}_5$/$C_6\mathbf{H}_4$), 7.57 (t. $^3J_{HH}$ = 8.0 Hz, 2H of $C_6\mathbf{H}_5$/$C_6\mathbf{H}_4$), 7.39-7.33 (m, 2H of $C_6\mathbf{H}_5$/$C_6\mathbf{H}_4$), 7.28-7.25 (m, 2H of $C_6\mathbf{H}_5$/$C_6\mathbf{H}_4$), 4.98 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 8.5 Hz, 1H, $C\mathbf{H}H'NO_2$), 4.91 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, $CH\mathbf{H}'NO_2$), 4.60 (td, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, $C\mathbf{H}$=CH_2NO_2), 3.96 (d, $^2J_{HH}$ = 8.5 Hz, 1H, $C\mathbf{H}(CO_2Me)_2$), 3.72 (s, 3H, $C\mathbf{H}_3$), 3.53 (s, 3H, $C'\mathbf{H}_3$); $^{13}C\{^1H\}$ (125 MHz) 167.9 (s, $\mathbf{C}O_2Me$), 167.4 (s, $\mathbf{C}'O_2Me$), 164.9 (s, $\mathbf{C}(O)Ph$), 149.0, 134.1, 130.5, 129.6, 129.1, 129.0, 128.7, 128.3, 126.6, 123.6 (10 × s, $\mathbf{C}_6H_5$/$\mathbf{C}_6H_4$), 76.6 (s, $\mathbf{C}H_2NO_2$), 53.8 (s, $\mathbf{C}H(CO_2Me)_2$), 53.1 (s, $\mathbf{C}O_2Me$), 53.1 (s, $\mathbf{C}'O_2Me$), 36.7 (s, $\mathbf{C}H$=CH_2-NO_2). IR (neat oil, cm^{-1}): 2955 (w), 1732 (vs), 1555 (s), 1213 (s), 708 (vs). Anal. Calcd. for $C_{20}H_{19}NO_8$ (401.37): C 59.85, H 4.77, N 3.49; found C 59.59, H 4.80, N 3.40.

Enantiomeric excesses were determined by HPLC (see Figure s14) with a Chiralpak AD column (90:10 v/v hexane/isopropanol, 1.0 mL/min, λ = 220 nm); for all catalysts t_R = 15.5-15.7 min (major), 26.0-26.3 min (minor).[s20]

Dimethyl 2-(2-nitro-1-(2-benzyloxyphenyl)ethyl)malonate (6jc). This new compound was isolated as a colorless oil per the general procedures for Scheme 4. NMR ($CDCl_3$, δ in ppm):[s22] ^{1}H (500 MHz) 7.47 (d, J = 7.5 Hz, 2H of $C_6\mathbf{H}_5/C_6\mathbf{H}_4$), 7.42 (t, 7.5 Hz, 2H of $C_6\mathbf{H}_5/C_6\mathbf{H}_4$), 7.36 (t, J = 7.5 Hz, 1H of $C_6\mathbf{H}_5/C_6\mathbf{H}_4$), 7.24 (t, J = 7.5 Hz, 1H of $C_6\mathbf{H}_5/C_6\mathbf{H}_4$), 7.17 (d, J = 7.5 Hz, 1H of $C_6\mathbf{H}_5/C_6\mathbf{H}_4$), 6.93 (d, J = 8.5 Hz, 1H of $C_6\mathbf{H}_5/C_6\mathbf{H}_4$), 6.89 (t, J = 7.5 Hz, 1H of $C_6\mathbf{H}_5/C_6\mathbf{H}_4$); 5.13 (d, $^3J_{HH}$ = 2.5 Hz, 2H, $C\mathbf{H}_2$Ph), 5.05 (dd, J = 13.0 Hz, J = 4.5 Hz, 1H, C**H**H'-NO_2), 4.84 (dd, J = 13.0 Hz, J = 4.5 Hz, 1H, CH**H**'NO_2), 4.44 (td, $^3J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 4.5 Hz, 1H, C**H**=CH_2NO_2), 4.17 (d, $^3J_{HH}$ = 9.5 Hz, 1H, C**H**$(CO_2Me)_2$), 3.72 (s, 3H, $C\mathbf{H}_3$), 3.50 (s, 3H, C'$\mathbf{H}_3$); ^{13}C (125 MHz) 168.3, (s, $\mathbf{C}O_2$Me), 167.7 (s, C'O_2Me), 156.7, 136.5, 130.9, 129.8, 128.9, 128.3, 127.7, 123.9, 121.2, 112.4 (10 × s, $\mathbf{C}_6H_4/\mathbf{C}_6H_5$), 76.0 (s, $\mathbf{C}H_2NO_2$), 70.6 ($\mathbf{C}H_2$Ph), 53.0 (s, $\mathbf{C}H(CO_2Me)_2$), 52.7 (s, $\mathbf{C}H_3$), 52.6 (s, C'H_3), 40.5 (s, $\mathbf{C}H{=}CH_2NO_2$). IR (neat oil, cm^{-1}): 3034 (w), 2955 (w), 2886 (w), 1732 (vs), 1553 (vs), 1238 (vs), 752 (s), 696 (m). Anal. Calcd. for $C_{20}H_{21}NO_7$ (387.38): C 62.01, H 5.46, N 3.62; found C 62.25, H 5.46, N 3.57.

Enantiomeric excesses were determined by HPLC (see Figure s15) with a Chiralcel OD column (90:10 v/v hexane/isopropanol, 1.0 mL/min, λ = 220 nm); for all catalysts t_R = 12.2-12.4 min (minor), 23.7-24.0 min (major).[s20]

Dimethyl 2-(2-nitro-1-furylethyl)malonate (6kc).[s23a,b] This known compound was isolated as a yellowish oil per the general procedures for Scheme 4. NMR ($CDCl_3$, δ in ppm):[s22] ^{1}H (500 MHz) 7.33 (m, 1H of $C_4\mathbf{H}_3O$), 6.28 (m, 1H of $C_4\mathbf{H}_3O$), 6.21 (d, $^3J_{HH}$ = 3.5 Hz, 1H of $C_4\mathbf{H}_3O$), 4.89 (m, 2H, $C\mathbf{H}_2NO_2$), 4.39 (td, $^3J_{HH}$ = 17.5 Hz, $^3J_{HH}$ = 12.5 Hz, 1H, C**H**=CH_2NO_2), 3.93 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C**H**$(CO_2Me)_2$), 3.75 (s, 3H, $C\mathbf{H}_3$), 3.68 (s, 3H, C'$\mathbf{H}_3$); ^{13}C{^{1}H} (125 MHz) 167.6 (s, $\mathbf{C}O_2$Me), 167.3 (s, C'O_2Me), 149.5, 143.0, 110.7, 106.5 (4 × s, $\mathbf{C}_4H_3O$), 75.4 (s, $\mathbf{C}H_2NO_2$), 53.2 (s, $\mathbf{C}H_3$), 53.1 (s, C'H_3), 52.8 (s, $\mathbf{C}H(CO_2Me)_2$), 36.9 (s, $\mathbf{C}H{=}CH_2NO_2$).

Enantiomeric excesses were determined by HPLC (see Figure s16) with a Chiralcel OD column (90:10 v/v hexane/isopropanol, 1.0 mL/min, λ = 220 nm); for all catalysts t_R = 11.8-12.0 min (minor), 28.7-29.0 min (major).[s20]

Dimethyl 2-(2-nitro-1-propylethyl)malonate (6lc).[s25] This known compound was iso-

lated as a colorless oil per the general procedures for Scheme 4. NMR ($CDCl_3$, δ in ppm):[s22] ^1H (500 MHz) 4.69 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 8.5 Hz, 1H, C**H**H'NO_2), 4.52 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 6.5 Hz, 1H, CH**H**'NO_2), 3.762 (s, 3H, OC**H**$_3$), 3.756 (s, 3H, OC'**H**$_3$), 3.66 (d, $^3J_{HH}$ = 6.0 Hz, 1H, C**H**$(CO_2Me)_2$), 2.90 (sext, $^3J_{HH}$ = 6.5 Hz, 1H, C**H**=CH_2NO_2), 1.46-1.34 (m, 4H, C**H**$_2$-C**H**$_2$), 0.92 (t, $^3J_{HH}$ = 7.5 Hz, 3H, C**H**$_3$); $^{13}C\{^1H\}$ (125 MHz) 168.5 (s, **C**O_2Me), 168.3 (s, **C**'O_2Me), 76.7 (s, **C**H_2NO_2), 53.0 (s, O**C**H_3), 52.9 (s, O**C**'H_3), 52.4 (s, **C**$H(CO_2Me)_2$), 36.9 (s, **C**H=CH_2NO_2), 32.3 (s, **C**$H_2CH_2CH_3$), 20.0 (s, CH_2**C**H_2CH_3), 13.9 (s, **C**H_3).

Enantiomeric excesses were determined by HPLC (see Figure s17) with a Chiralcel OD column (97.5:2.5 v/v hexane/isopropanol, 1.0 mL/min, λ = 220 nm); for (*S*,*S*)-**3**$^{3+}$ 2$BF_4^-$$BAr_f^-$ (newer column), t_R = 12.4 min (minor), 20.3 min (major); for Λ-(*S*,*S*)-**3**$^{3+}$ 3BF_4^- (older column), t_R = 9.7 min (minor), 18.8 min (major).[s20]

***N,N'*-Bis(*t*-butoxycarbonyl)-1-hydrazino-2-oxocyclopentanecarboxylic acid ethyl ester (9a).**[s26a] This known compound was obtained as a colorless oil per the general procedure for Scheme 5. NMR ($CDCl_3$, δ in ppm): ^1H (500 MHz) 6.51 (br s, 1H, N**H**), 4.32-4.16 (m, 2H, C**H**$_2$$CH_3$), 2.95-1.86 (m, 6H, 3 × ring C**H**$_2$), 1.57-1.33 (m, 18H, C(C**H**$_3$)$_3$ and C'(C'**H**$_3$)$_3$), 1.25 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_2C**H**$_3$); $^{13}C\{^1H\}$ (125 MHz) 205.6 (s, (**C**=O)CH_2), 167.3 (s, (**C**=O)OEt), 155.1 and 154.3 (2s, (**C**=O)O-t-Bu and (**C**'=O')O'-t-Bu'), 82.7 and 81.4 (2s, **C**$(CH_3)_3$ and **C**'$(C'H_3)_3$), 62.1 (s, **C**H_2CH_3), 35.9 (s), 32.0 (s), 28.1 and 28.0 (2s, C$(CH_3)_3$ and C′(**C**′$H_3)_3$), 27.7 (s), 18.4 (s), 14.0 (s, CH_2**C**H_3).

Enantiomeric excesses were determined by HPLC (see Figure s18) with a Chiralpak AD column (96:4 v/v hexane/isopropanol, 1.0 mL/min, λ = 210 nm); for Λ-(*S*,*S*)-**3**$^{3+}$ 2$Cl^-$$BAr_f^-$, t_R = 11.2 min (minor), 14.5 min (major); for Δ-(*S*,*S*)-**3**$^{3+}$ 2$Cl^-$$BAr_f^-$, t_R = 11.4 min (major), 15.8 min (minor).[s26a,s27]

***N,N'*-Bis(*t*-butoxycarbonyl)-1-hydrazino-2-oxocyclohexanecarboxylic acid ethyl ester (9b).**[s26] This known compound was obtained as a colorless oil per the general procedure for Scheme 5. NMR ($CDCl_3$, δ in ppm): ^1H (500 MHz) 6.51 (br s, 1H, N**H**), 4.33-4.12 (m, 2H, C**H**$_2$$CH_3$), 2.92-1.81 (m, 8H, 4 × ring C**H**$_2$), 1.52-1.37 (m, 18H, C(C**H**$_3$)$_3$ and C'(C'**H**$_3$)$_3$), 1.28-

1.22 (m, 3H, $CH_2C\mathbf{H}_3$); $^{13}C\{^1H\}$ (125 MHz) 205.4 (s, (**C**=O)CH_2), 169.4 (s, (**C**=O)OEt), 155.1 and 154.3 (2s, (**C**=O)O-t-Bu and (**C**'=O')O'-t-Bu'), 82.7 and 81.4 (2s, **C**$(CH_3)_3$ and **C**′$(C'H_3)_3$), 62.1 (s, **C**H_2CH_3), 38.0 (s), 35.8 (s), 34.7 (s), 28.1 and 28.0 (2s, C$(\mathbf{C}H_3)_3$ and C′$(\mathbf{C}'H_3)_3$), 20.9 (s), 18.4 (s), 14.0 (s, $CH_2\mathbf{C}H_3$).

Enantiomeric excesses were determined by HPLC (see Figure s19) with a Chiralpak AS-H column (99:1 v/v hexane/isopropanol, 1.0 mL/min, λ = 210 nm); for Λ-(*S*,*S*)-**3**$^{3+}$ 2Cl$^-$BAr$_f^-$, t_R = 9.7 min (major), 12.6 min (minor); for Δ-(*S*,*S*)-**3**$^{3+}$ 2Cl$^-$BAr$_f^-$, t_R = 9.6 min (minor), 11.6 min (major).[s26b,s27]

Crystallography. A (Λ-(*S*,*S*)-3^{3+} 3Cl$^-$·2H$_2$O·2CH$_3$OH). A solution of Λ-(*S*,*S*)-**3**$^{3+}$ 3Cl$^-$ in CH_3OH/H_2O (2:1 v/v) was allowed to slowly concentrate at room temperature. After 3 d, orange rods were collected. Data were obtained as noted in Table s1. Cell parameters were determined from 60 data frames taken at 0.5° widths. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.[s28] Data were corrected for Lorentz, polarization, and crystal decay effects. The program SADABS[s29] was used to correct for absorption effects. The structure was solved by direct methods using SHELXTL (XS).[s30] For each cobalt atom, two molecules of both H_2O and CH_3OH were located. Hydrogen atoms were placed in idealized positions and refined using a riding model. Non-hydrogen atoms were refined with anisotropic thermal parameters. The thermal ellipsoids of the carbon atoms of two phenyl rings showed significant elongation, indicating disorder. This was successfully modeled (C2B/C, C3B/C, C4B/C, C5B/C, C6B/C, C7B/C, 61:39 occupancy ratio; C9A/E, C10A/E, C11A/E, C12A/E, C13A/E, and C14A/E, 53:47 occupancy ratio). The parameters were refined by weighted least squares refinement on F^2 to convergence.[s30,s31] The absolute stereochemistry was confirmed (absolute structure parameter = 0.000(12); Table s1).[s32] **B (Δ-(*R*,*R*)-3^{3+} 3Cl·H$_2$O·3CH$_3$OH).** A solution of Δ-(*R*,*R*)-**3**$^{3+}$ 3Cl$^-$ in CH_3OH was allowed to slowly concentrate at room temperature. After 5 d, orange rods were collected. Data were obtained as noted in Table s1. Cell parameters were determined from 180 data frames taken at 0.5° widths. Integrated intensity information for each reflection was obtained by reduction of the data frames with the prog-

ram APEX2.[s28] Data were corrected for Lorentz, polarization, and crystal decay effects. The program SADABS[s29] was used to correct for absorption effects. The structure was solved by direct methods using SHELXTL (XS).[s30] For each cobalt atom, one molecule of water and ca. three molecules of CH_3OH were located. The thermal ellipsoids associated with one CH_3OH molecule indicated partial occupancy, which refined to 0.88; this value was fixed for the final refinement. Hydrogen atoms were placed in idealized positions and refined using a riding model. Non-hydrogen atoms were refined with anisotropic thermal parameters. The thermal ellipsoids of the carbon atoms of one phenyl ring indicated disorder. This refined to a 76:24 occupancy ratio (C30/30A, C31/31A, C32/32A, C33/33A, C34/34A, C35/35A). The ellipsoids of the disordered atoms were constrained. The parameters were refined by weighted least squares refinement on F^2 to convergence.[s30,s31] The absolute stereochemistry was confirmed (absolute structure parameter = 0.012 (4); Table s1).[s32] **C (Δ-(*S*,*S*)-3^{3+} 3Cl$^-$·12.5H$_2$O).** A solution of crude Δ-(*S*,*S*)-**3**$^{3+}$ 3Cl$^-$ (obtained from the Dowex column and containing some Λ diastereomer) in hot H_2O was allowed to slowly concentrate at room temperature. After 7 d, orange blocks were collected. Data were obtained as noted in Table s1. Cell parameters were determined from 180 data frames taken at 0.5° widths. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.[s28] Data were corrected for Lorentz, polarization, and crystal decay effects. The program SADABS[s29] was used to correct for absorption effects, and the structure was solved using SHELXTL (XS).[s30] The asymmetric unit contained two unique Δ-(*S*,*S*)-**3**$^{3+}$ moieties ($Z = 4$; $Z' = 2$) and 25 molecules of water. Hydrogen atoms were placed in idealized positions and refined using a riding model. All non-hydrogen atoms were refined with anisotropic thermal parameters. Several atoms yielded non-positive definite matrices and some exhibited elongated thermal ellipsoids. Strong constraints (listed in the Validation Response Form of the CHECKCIF file) were placed to keep the thermal ellipsoids meaningful. The parameters were refined by weighted least squares refinement on F^2 to convergence.[s30,s31] Platon[s33] was used to verify the absence of additional symmetry and voids. The absolute stereochemistry was confirmed (absolute structure parameter = 0.069(4); Table s1).[s32]

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(s3) This compound has been reported earlier in references s4a,b. In the former paper, no data were given for this salt, but the tris(perchlorate) salt Λ-(*S*,*S*)-**3**$^{3+}$ 3ClO_4^- was characterized by CD spectroscopy and microanalysis. The cobalt configuration was correctly assigned, but the carbon configurations were misassigned. In the latter paper, the cobalt and carbon configurations were established crystallographically following anion metathesis.

(s4) (a) Bosnich, B.; Harrowfield, J. MacB. *J. Am. Chem. Soc.* **1972**, *94*, 3425-3437. (b) Kuroda, R.; Mason, S. F. *J. Chem. Soc., Dalton Trans.* **1977**, *10*, 1016-1020.

(s5) Additional papers of historical relevance are as follows: (a) Gillard, R. D. *Tetrahedron* **1965**, *21*, 503-506. In this work, the carbon configurations were correctly assigned, but using salts with unspecified anions. There were no assignments of cobalt configurations. (b) Fereday, P. L.; Mason, S. F. *Chem. Commun.* **1971**, 1314-1315. In this work, the cobalt configurations were correctly assigned, but the carbon configurations misassigned, using CD spectra of salts with unspecified anions.

(s6) This complex has been previously reported, but no characterization was supplied (for the analogous complex of racemic **2** (a monohydrate), a microanalysis was given). See (a) Williams, O. F.; Bailar, Jr. J. C. *J. Am. Chem. Soc.* **1959**, *81*, 4464-4469 and especially the third paragraph on page 4467. (b) For the analogous perchlorate salt, see reference s4a. (c) An authentic sample was prepared by the procedure in reference s6a using (*S*,*S*)-**2**. Selected data: green powder. NMR (CD_3OD, δ in ppm): ^{1}H (500 MHz) 7.43-7.22 (m, 20H, Ph), 6.61 (d, $^3J_{HH}$ = 10 Hz, 4H, N**H**H'), 5.16 (br, 4H, NH**H'**), 4.87 (br s, CD_3O**H**/**H**$_2$O, 5H), 4.67 (s, 4H, C**H**NH_2); $^{13}C\{^1H\}$

(125 MHz) 138.8 (s, *i*), 130.2 (s, *o*),[s14] 129.9 (s, *p*), 128.7 (s, *m*),[s16] 66.8 (s, **C**HNH$_2$).

(s7) (a) Another CHPh signal was observed at δ 58.6 ppm, derived from the diprotonated ligand (*S*,*S*)-**2**. The intensity of this signal was disproportionate to its relative concentration (ca. × 2), as verified by spectra of independently prepared mixtures. (b) It is presumed that the intensities of signals due to Δ and Λ diastereomers are proportional to concentration.

(s8) These NMR solvents were not dried.

(s9) The degree of hydration was generally assigned by fitting the microanalytical data. Although the ^{1}H NMR spectra also showed OH signals, several factors can enhance their integrals. For example, in some cases the NMR solvents were not dried (so footnoted). In other cases, the NHH' protons undergo (partial) exchange with the deuterated solvent (so footnoted; CD_3OD will then give rise to a hydroxyl peak although acetone-d_6 should only give acetone-d_5).

(s10) Previous reports of this compound did not include microanalyses or any assignment of the degree of hydration.[s3-s5]

(s11) (a) This procedure was reported to give exclusively Δ-(*S*,*S*)-**3**$^{3+}$ 3ClO_4^- in reference s4a, but a yield was not quoted. (b) The Δ diastereomer was also isolated as a non-hydrated crystalline byproduct from the synthesis of Λ-(*S*,*S*)-**3**$^{3+}$ 3ClO_4^-, and characterized by microanalysis and CD spectroscopy. (c) In our hands, we repeatedly obtained 15-18% of the Λ diastereomer (four independent syntheses).

(s12) Robinson, W. R. *J. Chem. Ed.* **1985**, *62*, 1001.

(s13) No attempts were made to characterize the degree of hydration of salts that were mixtures of diastereomers (and thus of variable composition).

(s14) This compound was similarly prepared in reference s4a and characterized by microanalysis and CD spectroscopy. The degree of hydration was presumed to be identical.

(s15) The NH and/or NH' signal was not observed or was of reduced intensity due to H/D exchange.

(s16) The $^{13}C\{^1H\}$ signal with the chemical shift closest to benzene was assigned to the *meta* carbon atom: Mann, B. E. *J. Chem. Soc. Perkin Trans. 2* **1972**, 30-34.

(s17) With the exception of the least intense 129.2 ppm signal, the phenyl resonances of the minor Λ diastereomer appeared to overlap with those of the major Δ diastereomer.

(s18) A similar experiment has been mentioned in reference s4a, but without any quantitative details. The conversion is represented as 100% in the experimental section, and "at least 90%" in the text.

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(s20) The absolute configurations of **6aa**-**ac** were assigned by HPLC using conditions similar to those in the literature (see references s23c,d). Catalysts with Λ-(*S*,*S*) configurations gave predominantly *R* enantiomers. The dominant configurations of **6bc**-**6lc** were assigned assuming analogous relative retention times.

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(s27) The chiral HPLC column employed with **9a** featured the same stationary phase but a different particle size from that used earlier in the literature.[s26] It is presumed that the well separated enantiomers exhibit identical orders of elution, and configurations were assigned accordingly. The dominant configurations of **9b** were assigned assuming analogous relative retention

times.

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Table s1. Summary of crystallographic data for solvates of stereoisomers of $\mathbf{3}^{3+}$ $3Cl^{-}$.

Complex	Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $3Cl^{-}\cdot 2H_2O\cdot 2CH_3OH$	Δ-(*R*,*R*)-$\mathbf{3}^{3+}$ $3Cl^{-}\cdot H_2O\cdot 3CH_3OH$[a]	Δ-(*S*,*S*)-$\mathbf{3}^{3+}$ $3Cl^{-}\cdot 12.5H_2O$
empirical formula	$C_{44}H_{60}Cl_3CoN_6O_4$	$C_{44.88}H_{61.54}Cl_3CoN_6O_{3.88}$[a]	$C_{84}H_{146}Cl_6Co_2N_{12}O_{25}$[b]
formula weight	902.26	912.60	2054.69[b]
temperature of collection [K]	110(2)	110(2)	110(2)
diffractometer	Bruker APEX 2	Bruker GADDS	Bruker GADDS
wavelength [Å]	0.71073	1.54178	1.54178
crystal system	tetragonal	tetragonal	monoclinic
space group	P4(3)	P4(1)	P2(1)
unit cell dimensions:			
a [Å]	13.839(4)	13.8725(7)	12.0877(6)
b [Å]	13.839(4)	13.8725(7)	25.0985(14)
c [Å]	24.216(9)	24.3173(13)	16.8235(8)
α [deg]	90	90	90
β [deg]	90	90	90.887(3)
γ [deg]	90	90	90
V [Å^3]	4638(2)	4679.8(4)	5103.4(5)
Z	4	4	2[b]
ρ_{calc} [Mg/m^3]	1.292	1.295	1.337
Absorption coefficient [mm^{-1}]	0.590	4.822	4.607
F(000)	1904	1928	2180
crystal size [mm^3]	0.60 × 0.10 × 0.10	0.12 × 0.08 × 0.04	0.16 × 0.15 × 0.07
Θ [deg]	2.23 to 27.49	3.19 to 60.00	2.63 to 60.00
range / indices (*h*, *k*, *l*)	–17,17; –17,17; –31,31	–15,15; –15,15; –25,26	–13,13; –28,27; –18,18
reflections collected	70126	65183	112447
independent reflections	10535 [R(int) = 0.0425]	6282 [R(int) = 0.0647]	14790 [R(int) = 0.0916]
completeness to Θ = 27.49°	99.7%	98.5%	99.9%

absorption correction	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents
max. and min. transmission	0.9434 and 0.7187	0.8305 and 0.5953	0.7386 and 0.5260
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data / restraints / parameters	10535 / 7 / 525	6282 / 21 / 546	14790 / 265 / 1105
goodness-of-fit on F^2	1.059	1.071	1.149
final R indices [I>2σ(I)]	$R1$ = 0.0442, w$R2$ = 0.1171	$R1$ = 0.0407, w$R2$ = 0.0841	$R1$ = 0.0746, w$R2$ = 0.1791
R indices (all data)	$R1$ = 0.0501, w$R2$ = 0.1220	$R1$ = 0.0510, w$R2$ = 0.0871	$R1$ = 0.0807, w$R2$ = 0.1830
absolute structure parameter	0.000(12)	0.012(4)	0.069(5)
largest diff. peak and hole [e Å^{-3}]	0.945 / –0.255	0.362 / –0.622	0.972 / –0.698

[a]This salt is presented, for simplicity, as a tris(CH_3OH) solvate; however, as detailed in the experimental section, one CH_3OH molecule refined to an occupancy of 0.88. [b]For the asymmetric unit; see experimental section.

Table s2. Key interatomic distances (Å) and angles (°) in crystallographically characterized complexes.[a]

atoms	Λ-(*S*,*S*)-**3**$^{3+}$ 3Cl$^-$ ·2H_2O·2CH_3OH	Δ-(*S*,*S*)-**3**$^{3+}$ 3Cl$^-$ ·12.5H_2O[b]	Δ-(*S*,*S*)-**3**$^{3+}$ 3Cl$^-$ ·12.5H_2O[b]	Δ-(*R*,*R*)-**3**$^{3+}$ 3Cl$^-$ ·H_2O·3CH_3OH
Co1-N1	1.910(2)	1.967(6)	1.976(5)	1.962(3)
Co1-N2	1.975(3)	1.961(6)	1.959(6)	1.989(3)
Co1-N3	1.985(2)	1.954(5)	1.955(6)	1.957(3)
Co1-N4	1.963(2)	1.958(6)	1.950(6)	1.967(3)
Co1-N5	1.963(3)	1.963(6)	1.973(7)	1.989(3)
Co1-N6	1.949(3)	1.949(5)	1.963(6)	1.970(3)
N1-C1	1.492(4)	1.488(9)	1.501(9)	1.484(5)
N2-C8	1.511(4)	1.489(9)	1.505(9)	1.483(5)
N3-C15	1.509(3)	1.475(9)	1.486(9)	1.506(5)
N4-C22	1.502(4)	1.502(9)	1.495(9)	1.511(5)
N5-C29	1.498(4)	1.494(9)	1.491(10)	1.504(5)
N6-C36	1.506(4)	1.508(9)	1.489(10)	1.504(5)
N1···Cl1	3.194(3)	3.3604(1)	-	3.279(3)
N3···Cl1	3.428(3)	3.2343(2)	-	3.194(3)
N5···Cl1	3.269(3)	3.2762(1)	-	3.445(3)
N2···Cl3	3.259(3)	3.2403(1)	3.3656(1)	3.208(3)
N4···Cl3	3.198(3)	3.2363(1)	3.2062(2)	3.265(3)
N6···Cl3	3.195(3)	3.3277(2)	3.2268(1)	3.220(3)
N5···Cl2	3.231(3)	4.2407(2)	-	3.327(4)
N4···Cl2	3.266(3)	3.2458(2)	-	3.202(3)
N1H···Cl1	2.313	2.6254		2.437
N3H···Cl1	2.606	2.5448		2.346
N5H···Cl1	2.436	2.5689		2.634
N2H···Cl3	2.379	2.5258	2.6708	2.324
N4H···Cl3	2.376	2.4211	2.5065	2.379
N6H···Cl3	2.364	2.6166	2.4632	2.398
N5H···Cl2	2.386	3.8632	-	2.498
N4H···Cl2	2.387	2.4074	-	2.356
N3-Co1-N6	172.7(1)	175.2(2)	174.7(3)	172.66(14)
N1-Co1-N4	172.7(1)	175.5(2)	175.1(3)	171.66(13)
N2-Co1-N5	171.9(1)	175.3(2)	175.4(3)	171.62(14)

N3-Co1-N1	90.9(1)	92.3(2)	91.8(2)	90.95(14)
N3-Co1-N2	96.3(1)	91.4(2)	90.8(3)	94.98(14)
N3-Co1-N4	84.4(1)	84.4(2)	84.4(2)	84.56(13)
N3-Co1-N5	90.5(1)	92.7(2)	92.2(2)	91.07(13)
N6-Co1-N1	94.7(1)	92.1(2)	92.3(2)	94.39(14)
N6-Co1-N2	89.0(1)	91.0(2)	92.8(2)	90.60(14)
N6-Co1-N4	90.5(1)	91.3(2)	91.7(2)	90.74(13)
N6-Co1-N5	84.6(1)	85.1(2)	84.5(3)	83.87(12)
N1-Co1-N2	84.3(1)	84.7(2)	84.8(2)	83.76(14)
N2-Co1-N4	90.7(1)	92.3(2)	92.2(2)	89.62(14)
N4-Co1-N5	94.3(1)	90.5(2)	91.5(2)	96.72(14)
N5-Co1-N1	91.3(1)	92.7(2)	91.6(2)	90.37(14)
N1–H···Cl1	165.5	137.35		155.7
N3–H···Cl1	152.4	132.09		156.9
N5–H···Cl1	154.0	134.07		150.5
N2–H···Cl3	165.8	134.78	132.9	161.2
N4–H···Cl3	152.2	147.71	133.1	168.2
N6–H···Cl3	153.6	134.60	140.5	151.9
N5–H···Cl2	156.3	108.14	-	153.2
N4–H···Cl2	165.5	151.51	-	156.6

[a] The atoms are numbered such that for each salt, N1, N3, and N5 define one of the C_3 NH faces to which a chloride anion is hydrogen bonded, and N2, N4, and N6 the other. [b] These values are for one of the two independent trications in the unit cell. These are distinguished by a different H_2O hydrogen bonding pattern.

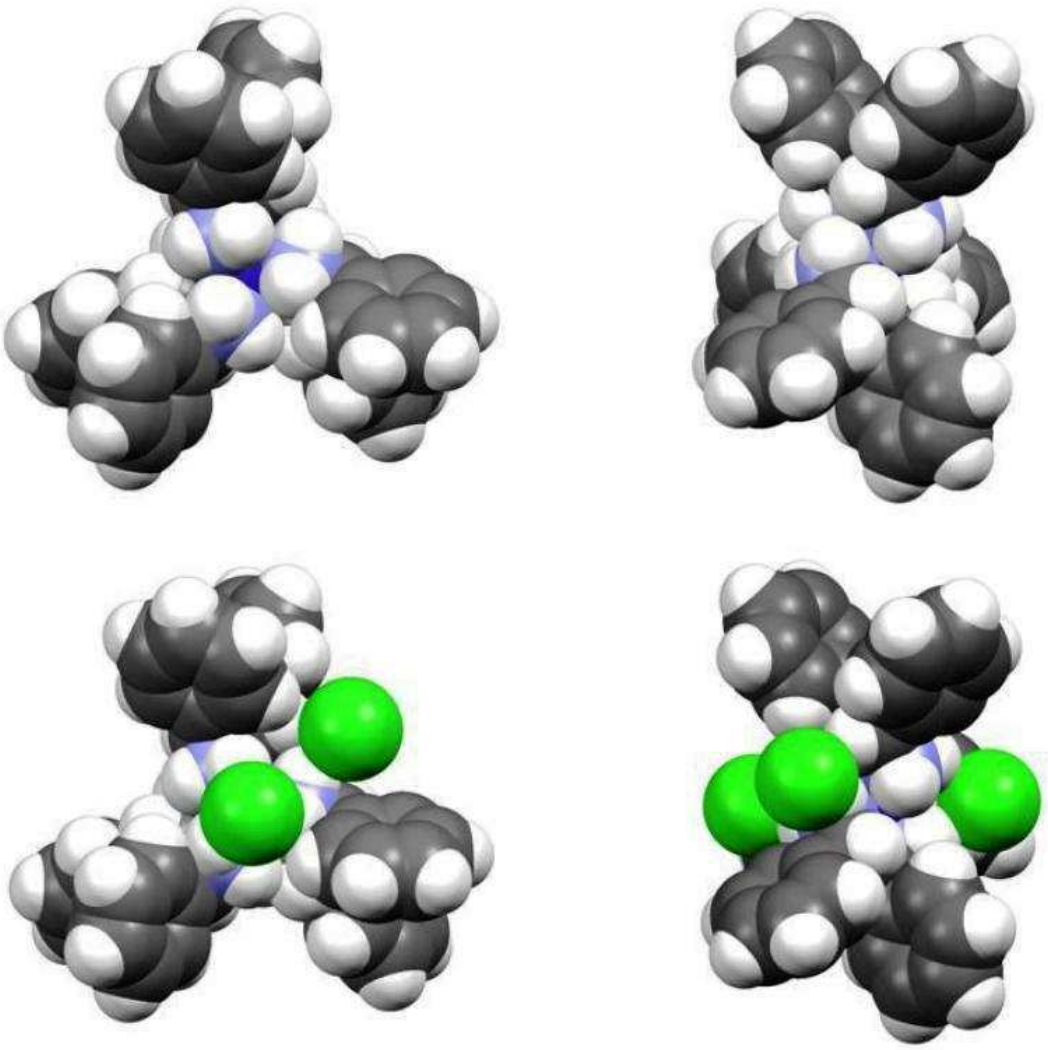


Figure s1. Thermal ellipsoid diagram (50% probability level) of Δ-(*S*,*S*)-**3**$^{3+}$ 3Cl^{-}·12.5H_2O with solvent molecules removed for clarity. Upper left and right, views down the idealized C_3 and C_2 axes with chloride ions omitted; lower left and right, analogous views with chloride ions.

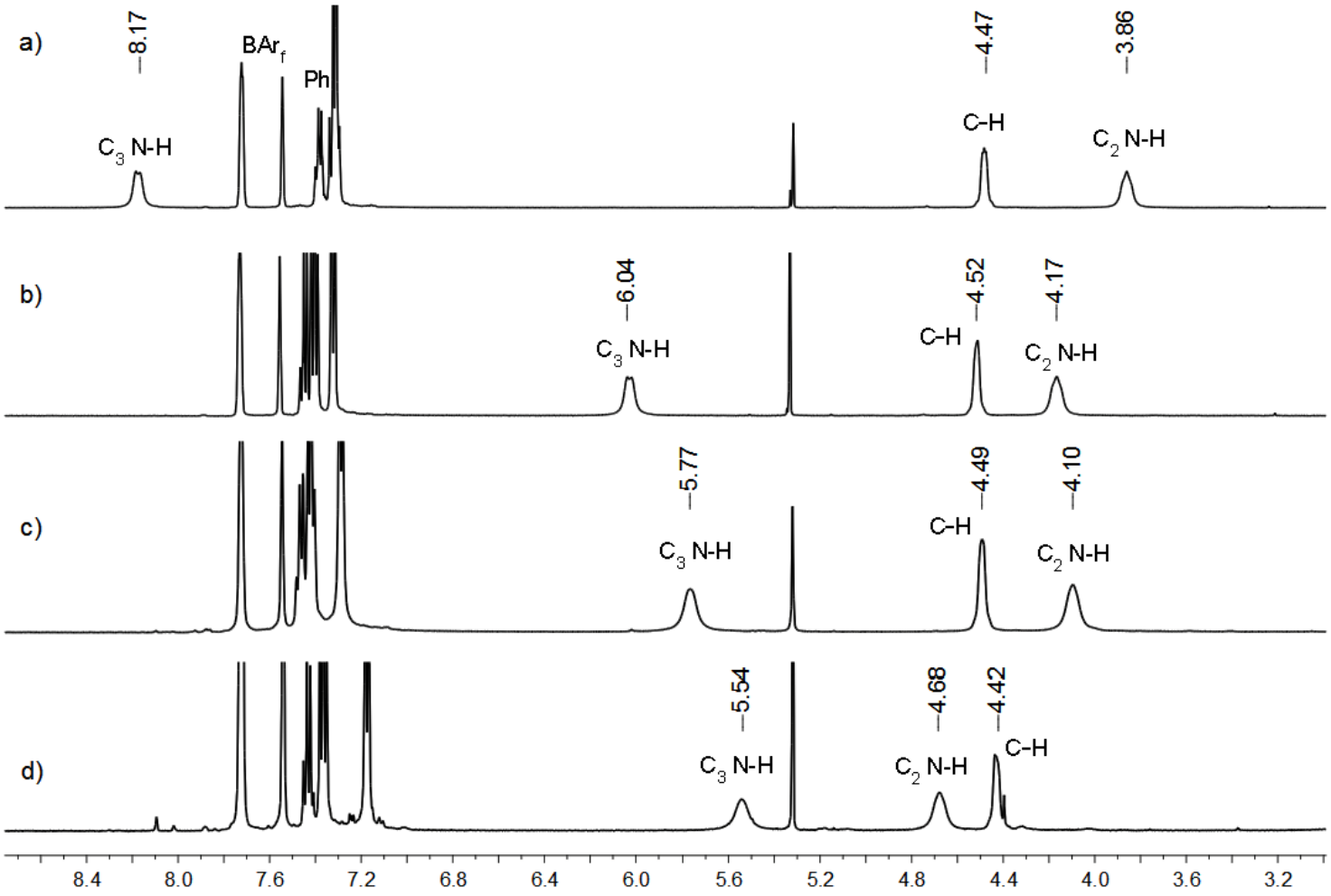


Figure s2. ^{1}H NMR spectra (CD_2Cl_2) of (a) Λ-(*S*,*S*)-**3**$^{3+}$ 2Cl$^-$BAr$_f^-$, (b) Λ-(*S*,*S*)-**3**$^{3+}$ 2BF$_4^-$BAr$_f^-$, (c) Λ-(*S*,*S*)-**3**$^{3+}$ 2PF$_6^-$BAr$_f^-$, and (d) Λ-(*S*,*S*)-**3**$^{3+}$ 3BAr$_f^-$.

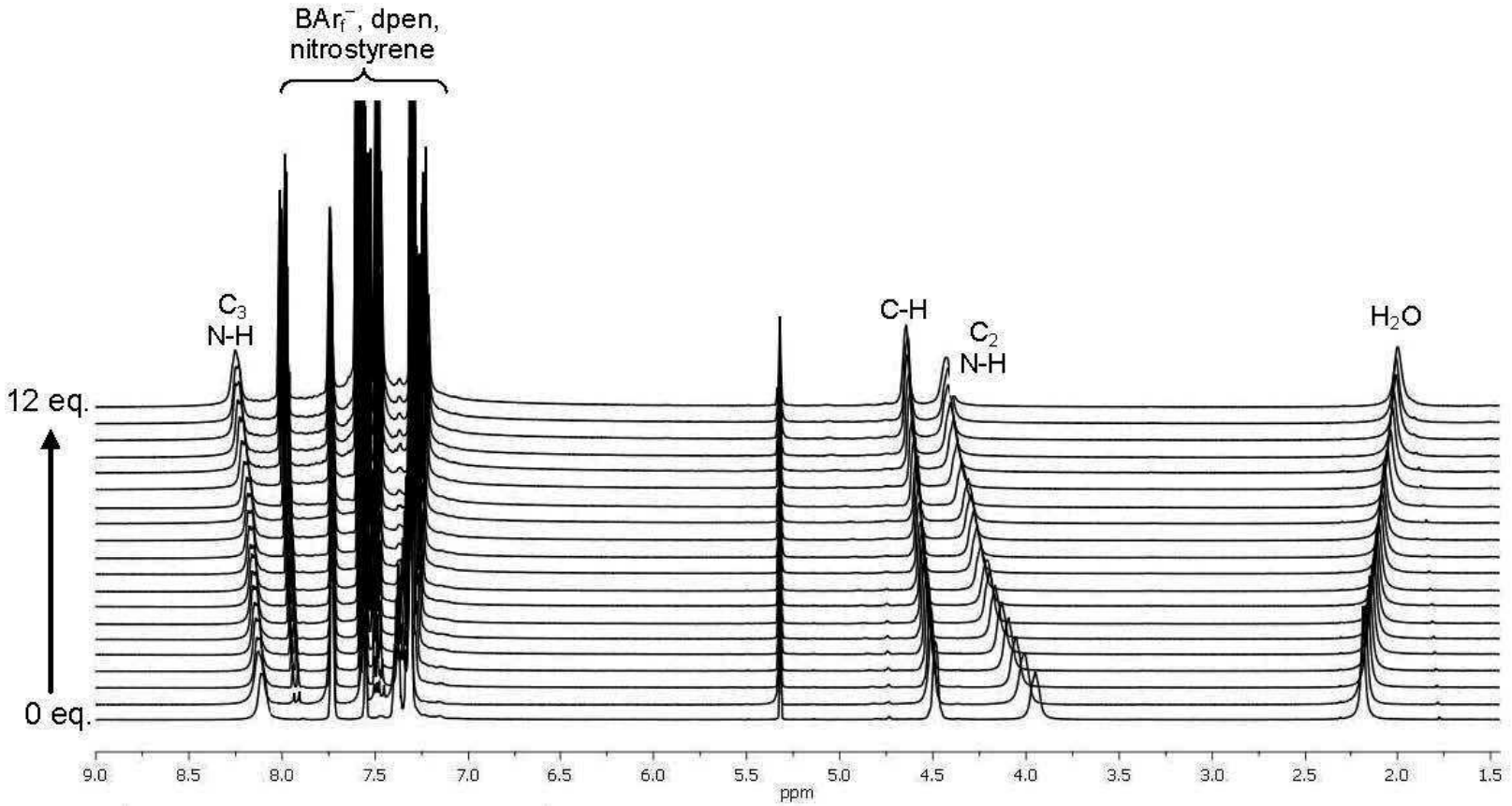
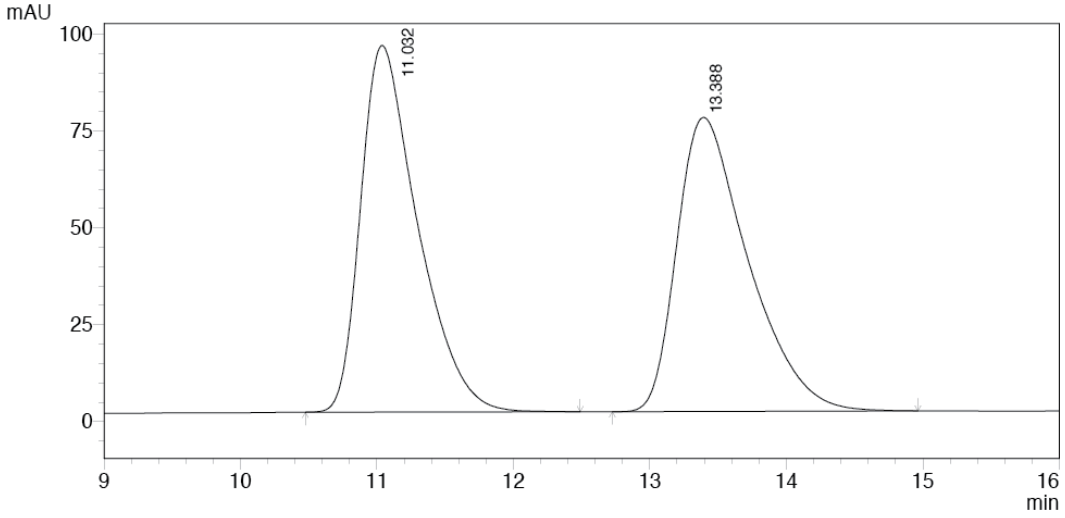


Figure s3. ^{1}H NMR spectra: titration of a CD_2Cl_2 solution of Λ-(*S*,*S*)-**3**$^{3+}$ 2Cl$^-$BAr$_f^-$ with *trans*-ß-nitrostyrene (**4a**). Data (equiv of **4a**/NH signals, δ in ppm): 0.25/4.010 and 8.127; 0.50/4.053 and 8.134; 0.75/4.094 and 8.141; 1.0/4.129 and 8.131; 1.25/4.165 and 8.155; 1.50/4.195 and 8.158; 1.75/4.204 and 8.162; 2.0/4.241 and 8.169; 2.50/4.28 and 8.179; 2.75/4.296 and 8.183; 3.0/4.31 and 8.178; 4.0/4.342 and 8.184; 5.0/4.368 and 8.196; 6.0/4.387 and 8.227; 7.0/4.405 and 8.236; 8.0/4.418 and 8.234; 9.0/4.432 and 8.249.

Diisopropyl 2-(2-nitro-1-phenylethyl)malonate (6a<u>a</u>).

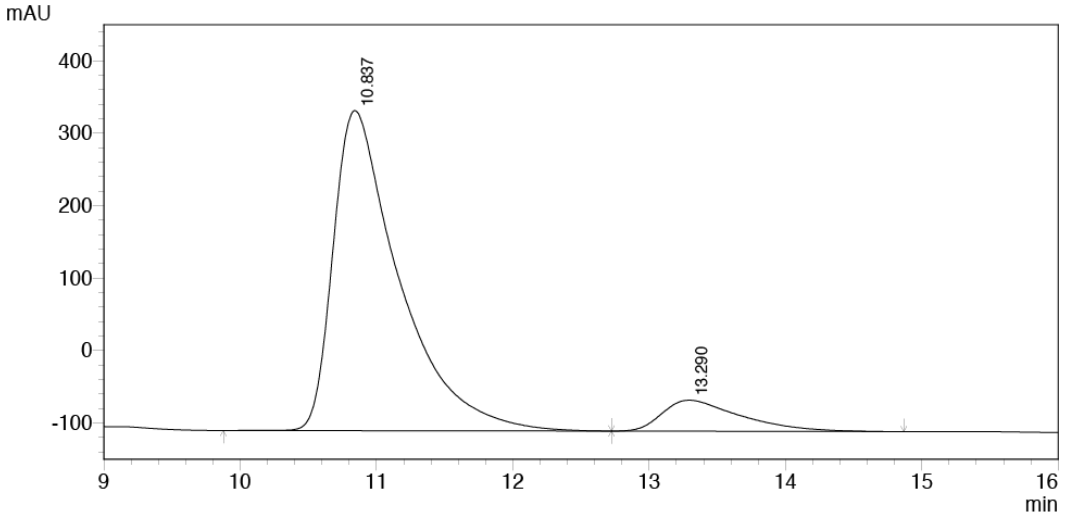
(a)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.032	2745001	94604	49.931	55.488
2	13.388	2752610	75890	50.069	44.512
Total		5497611	170494	100.000	100.000

(b)



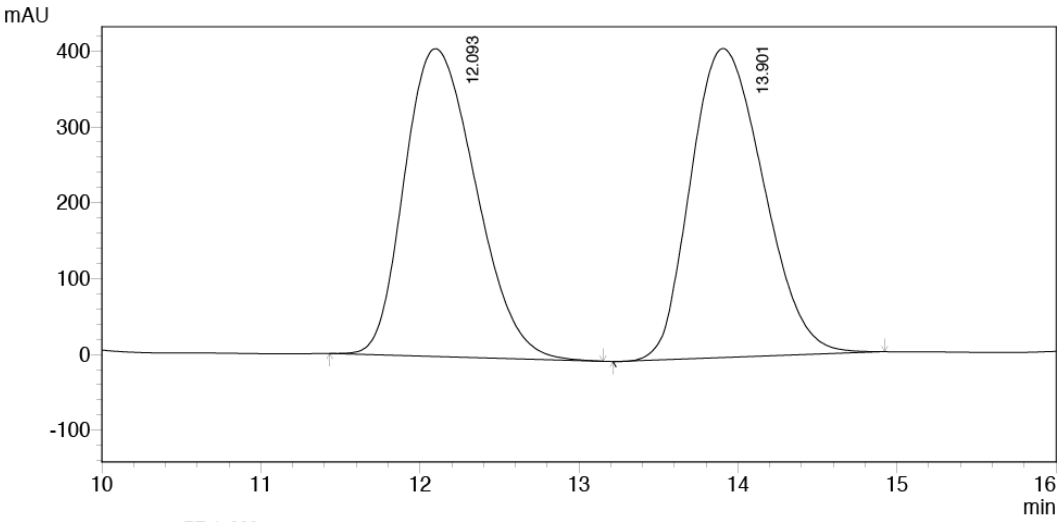
PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.837	14897274	441745	89.745	91.162
2	13.290	1702201	42826	10.255	8.838
Total		16599476	484571	100.000	100.000

Figure s4. HPLC traces of **6a<u>a</u>** (Scheme 3, entry 1): (a) racemic sample; (b) catalyzed by Λ-(*S*,*S*)-**3**$^{3+}$ 2Cl^{-}BAr$_f^{-}$.

Diethyl 2-(2-nitro-1-phenylethyl)malonate (6a<u>b</u>).

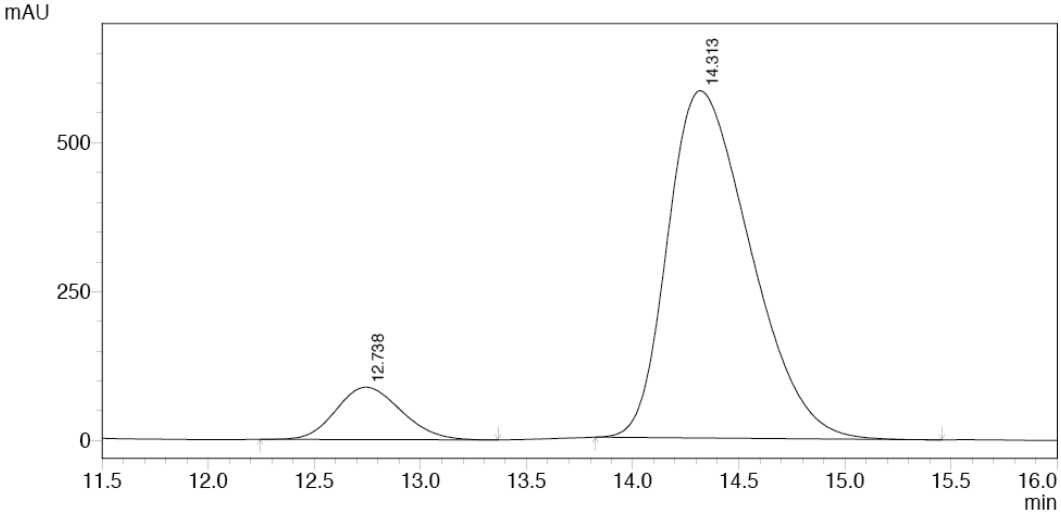
(a)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.093	12661766	405824	49.414	49.903
2	13.901	12962212	407395	50.586	50.097
Total		25623977	813219	100.000	100.000

(b)



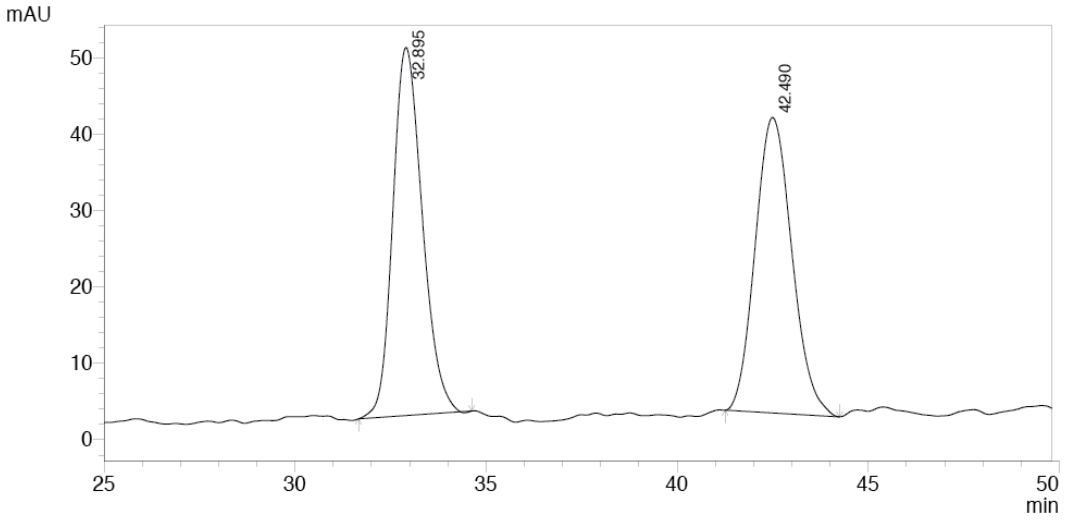
PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.738	1877941	87934	10.619	13.108
2	14.313	15806284	582897	89.381	86.892
Total		17684225	670831	100.000	100.000

Figure s5. HPLC traces of **6a<u>b</u>** (Scheme 3, entry 3): (a) racemic sample; (b) catalyzed by Λ-(*S*,*S*)-**3**$^{3+}$ 2Cl^{-}BAr$_f^{-}$.

Dimethyl 2-(2-nitro-1-phenylethyl)malonate (6ac).

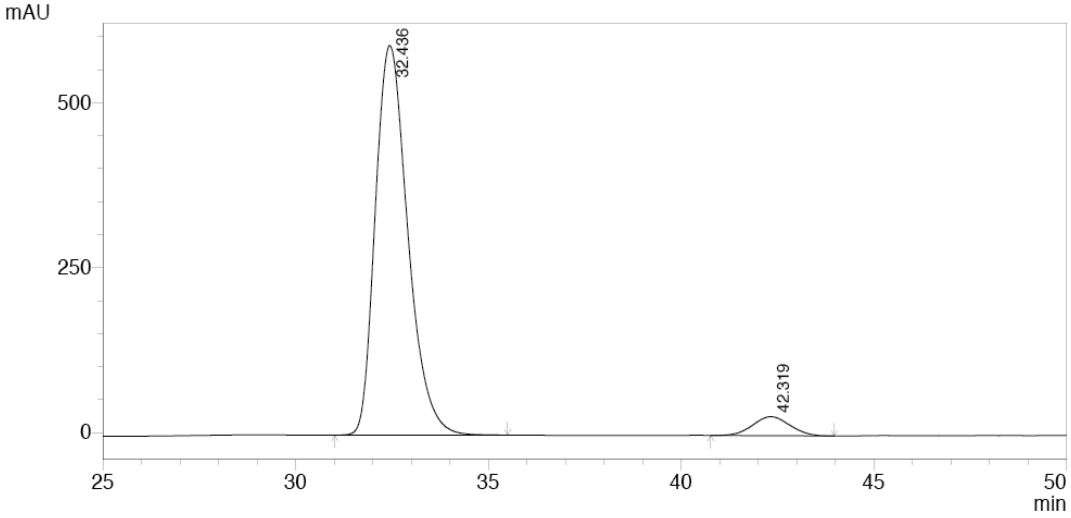
(a)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.895	2592054	48187	49.983	55.472
2	42.490	2593793	38681	50.017	44.528
Total		5185847	86867	100.000	100.000

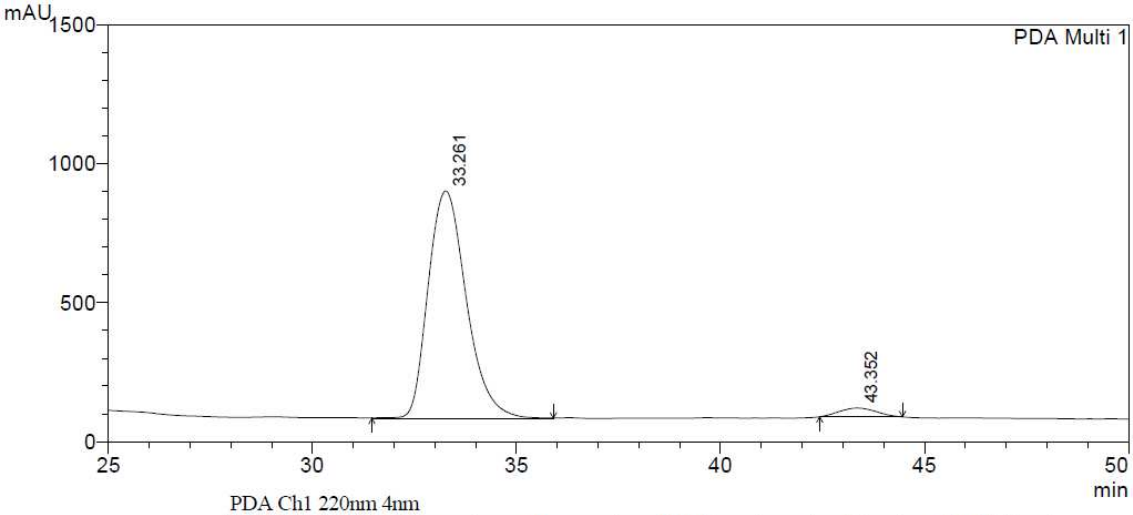
(b)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.436	34674163	590859	94.706	95.343
2	42.319	1938180	28862	5.294	4.657
Total		36612343	619722	100.000	100.000

(c)



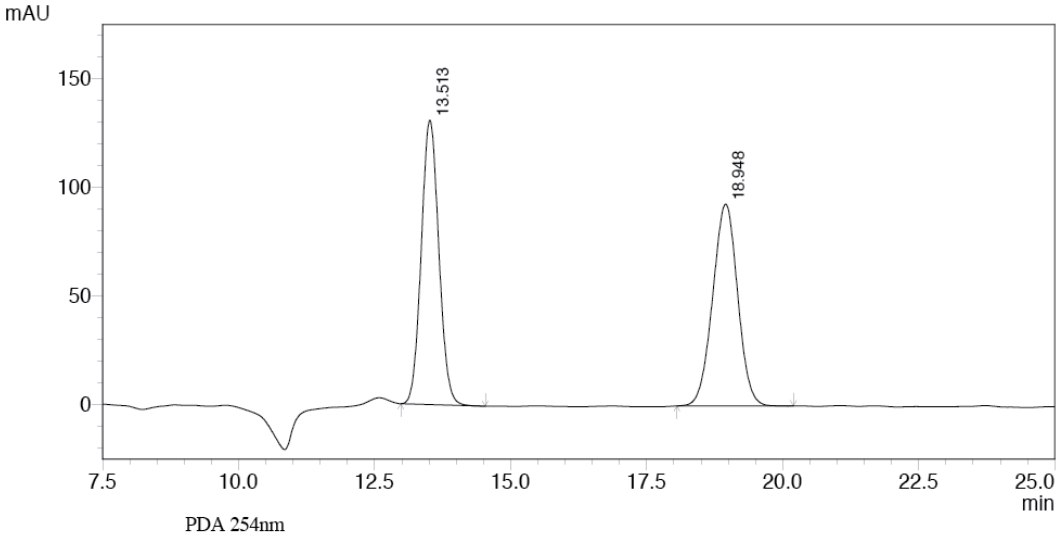
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.261	53520336	818591	96.395	96.248
2	43.352	2001490	31911	3.605	3.752
Total		55521826	850502	100.000	100.000

Figure s6. HPLC traces of **6ac** (Scheme 4, entry 1): (a) racemic sample; (b) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $2BF_4^-BAr_f^-$; (c) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}3BF_4^-$.

Dimethyl 2-(2-nitro-1-α-naphthylethyl)malonate (6bc).

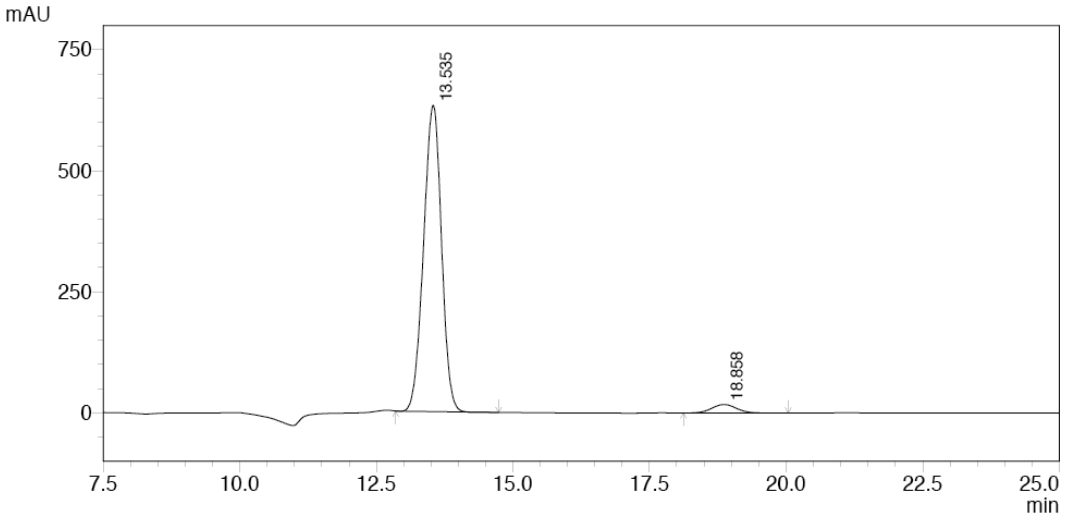
(a)



PDA 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.513	2941994	130912	49.780	58.498
2	18.948	2967956	92876	50.220	41.502
Total		5909950	223789	100.000	100.000

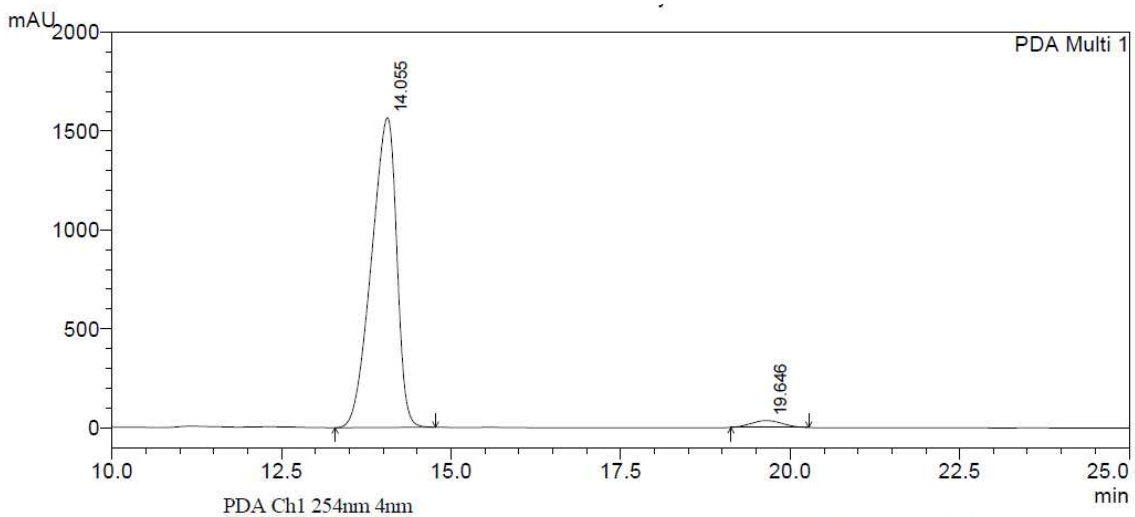
(b)



PDA 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.535	14427103	632667	96.261	97.288
2	18.858	560393	17639	3.739	2.712
Total		14987496	650305	100.000	100.000

(c)



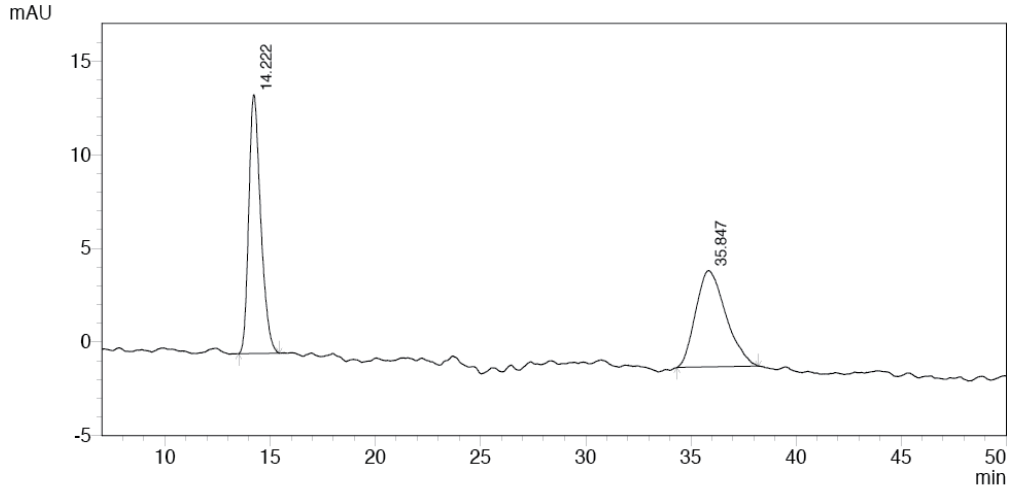
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.055	40487308	1566198	97.320	97.810
2	19.646	1114899	35065	2.680	2.190
Total		41602207	1601263	100.000	100.000

Figure s7. HPLC traces of **6bc** (Scheme 4, entry 2): (a) racemic sample; (b) catalyzed by Λ-(*S*,*S*)-**3**$^{3+}$ 2$BF_4^-$$BAr_f^-$; (c) catalyzed by Λ-(*S*,*S*)-**3**$^{3+}$3BF_4^-.

Dimethyl 2-(2-nitro-1-β-naphthylethyl)malonate (6cc).

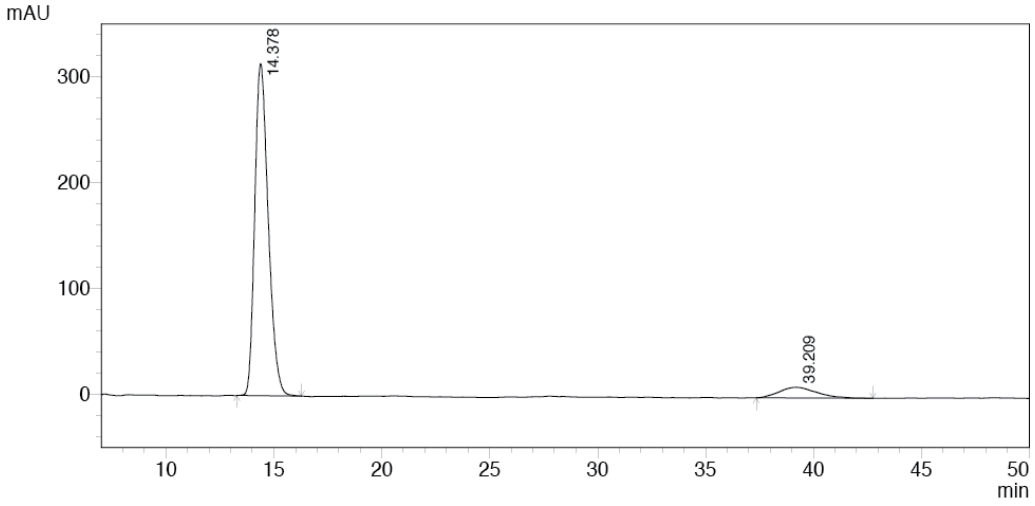
(a)



PDA 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.222	545650	13812	51.472	72.833
2	35.847	514433	5152	48.528	27.167
Total		1060083	18965	100.000	100.000

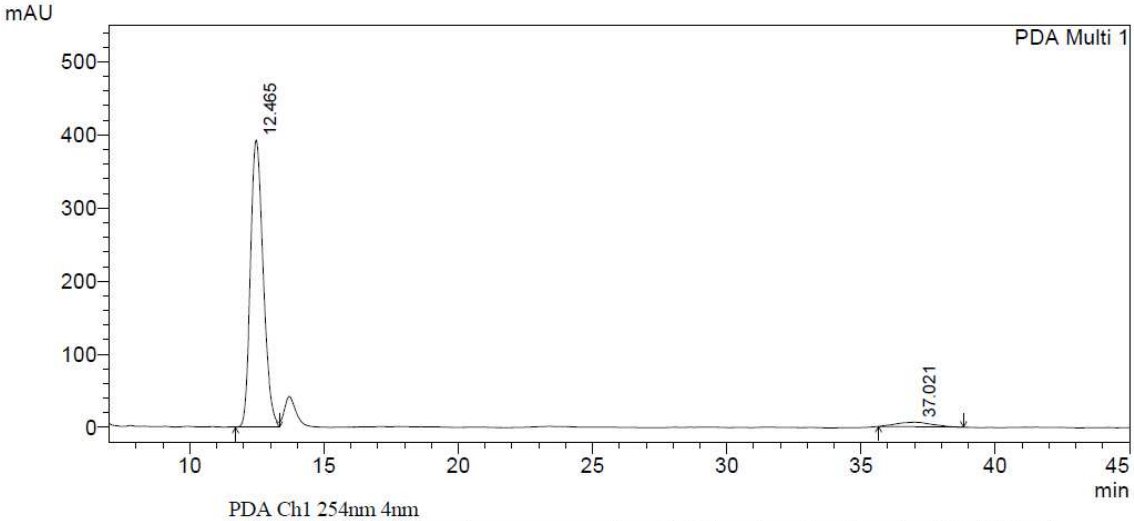
(b)



PDA 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.378	13650190	313478	91.924	96.896
2	39.209	1199200	10041	8.076	3.104
Total		14849390	323518	100.000	100.000

(c)



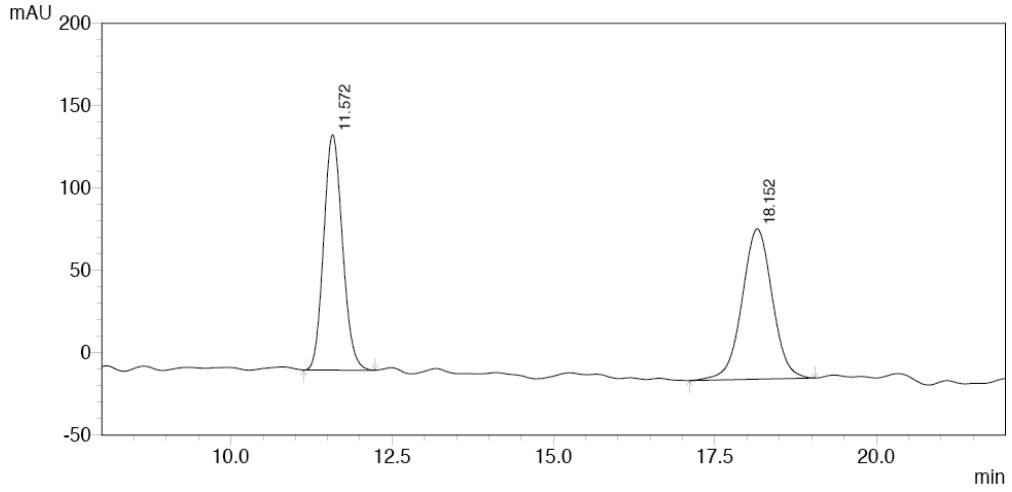
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.465	13013612	393149	95.892	98.467
2	37.021	557439	6123	4.108	1.533
Total		13571051	399272	100.000	100.000

Figure s8. HPLC traces of **6cc** (Scheme 4, entry 3): (a) racemic sample; (b) catalyzed by Λ-(*S*,*S*)-**3**$^{3+}$ 2$BF_4^-$$BAr_f^-$; (c) catalyzed by Λ-(*S*,*S*)-**3**$^{3+}$ 3BF_4^- (older column).

Dimethyl 2-(2-nitro-1-(4-methoxyphenyl)ethyl)malonate (6dc)

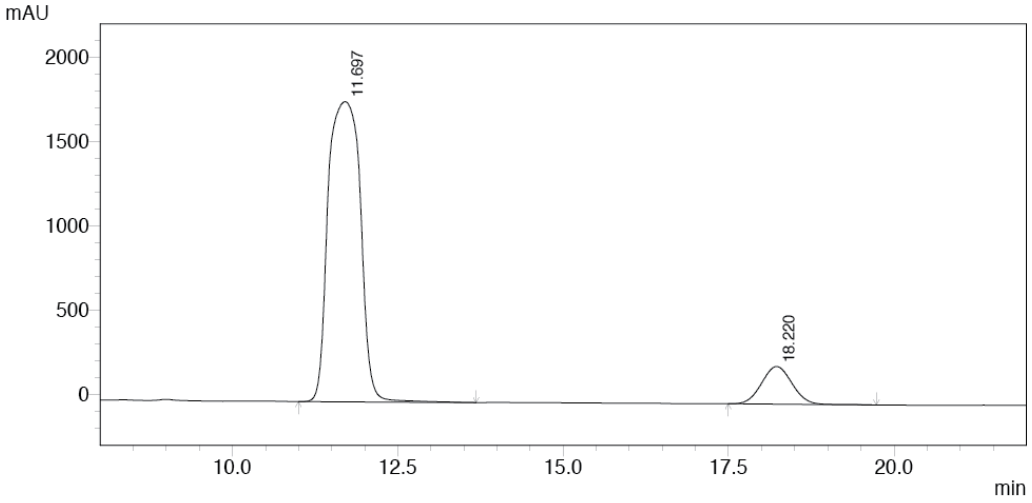
(a)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.572	2892734	142917	49.286	61.046
2	18.152	2976564	91196	50.714	38.954
Total		5869298	234114	100.000	100.000

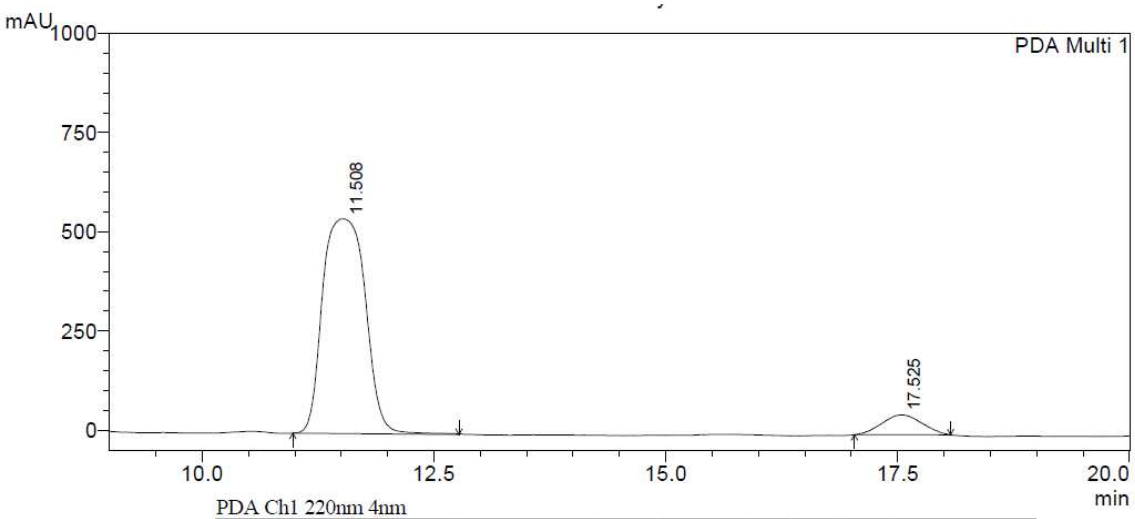
(b)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.697	60314078	1781389	89.351	88.845
2	18.220	7188616	223672	10.649	11.155
Total		67502694	2005061	100.000	100.000

(c)



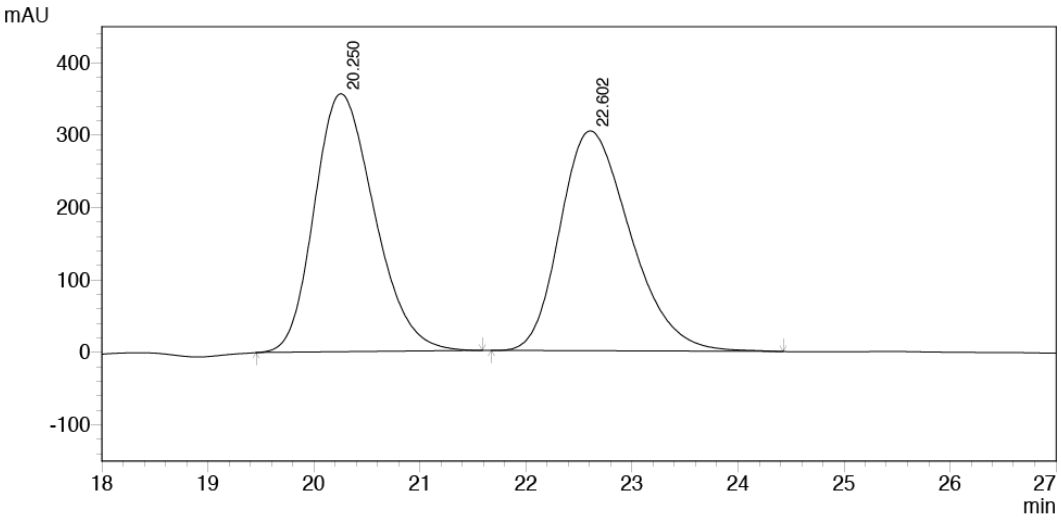
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.508	17303657	540750	92.054	91.598
2	17.525	1493635	49601	7.946	8.402
Total		18797292	590351	100.000	100.000

Figure s9. HPLC traces of **6dc** (Scheme 4, entry 4): (a) racemic sample; (b) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $2BF_4^-BAr_f^-$; (c) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $3BF_4^-$.

Dimethyl 2-(2-nitro-1-(3,4-dichlorophenyl)ethyl)malonate (6ec).

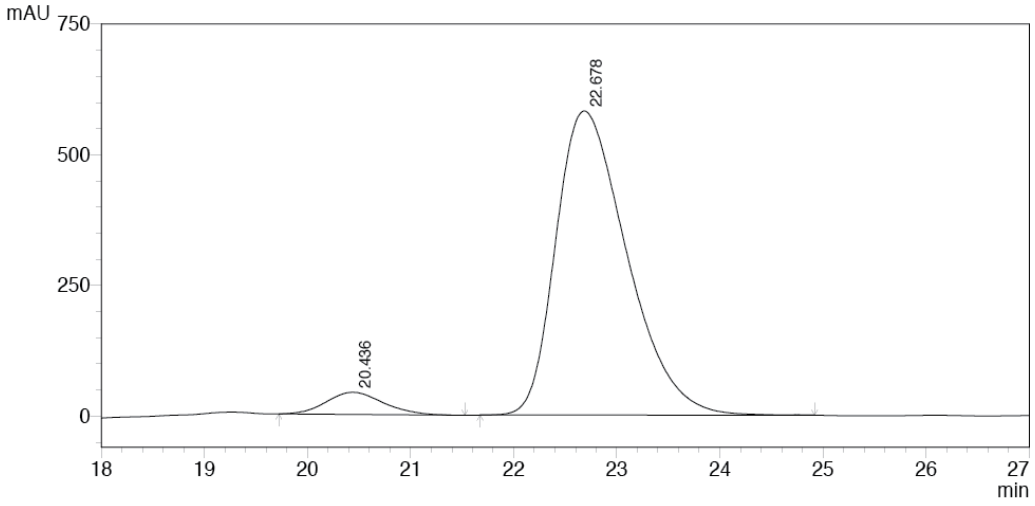
(a)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.250	14034598	356495	50.085	53.998
2	22.602	13986920	303708	49.915	46.002
Total		28021519	660203	100.000	100.000

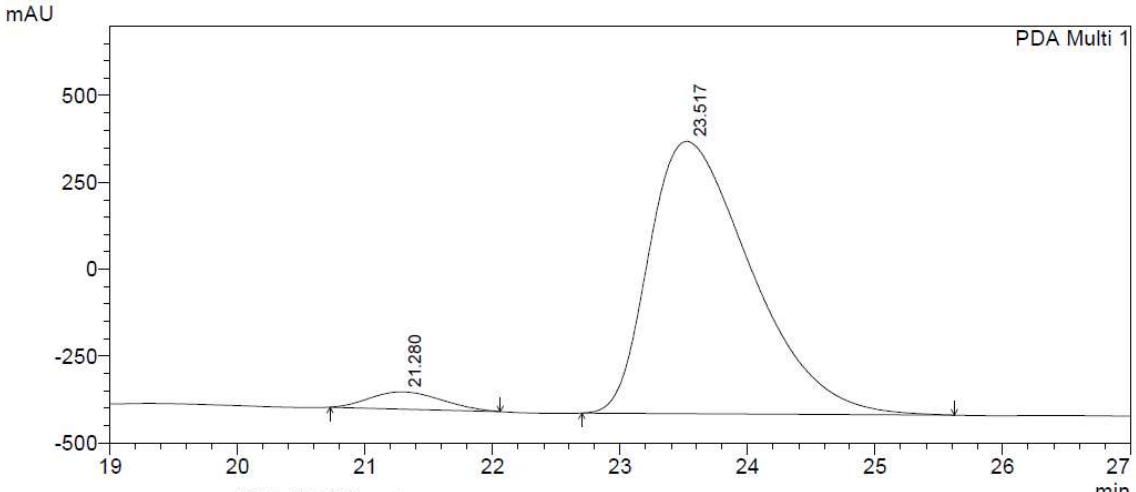
(b)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.436	1637581	42354	5.544	6.785
2	22.678	27899733	581886	94.456	93.215
Total		29537314	624240	100.000	100.000

(c)



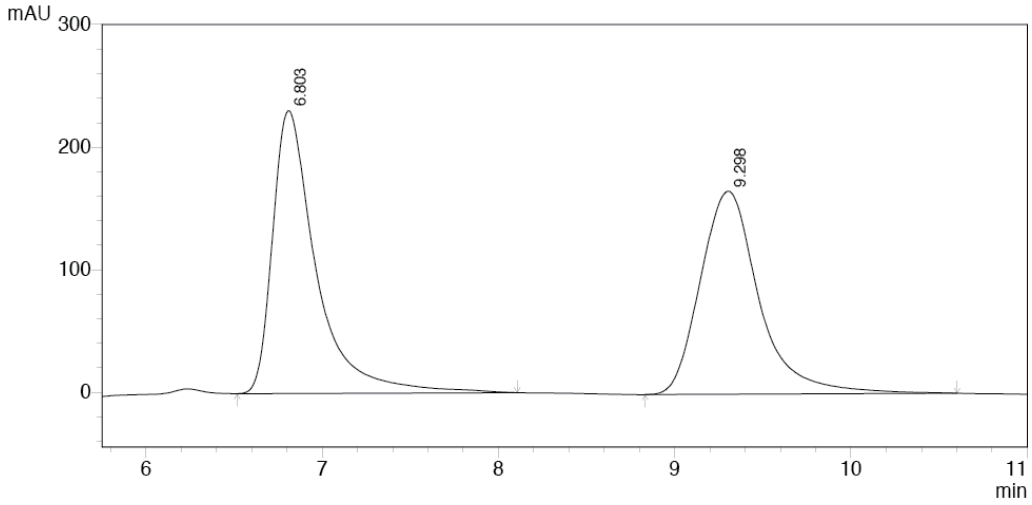
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.280	1936609	49425	4.245	5.932
2	23.517	43682241	783840	95.755	94.068
Total		45618850	833265	100.000	100.000

Figure s10. HPLC traces of **6ec** (Scheme 4, entry 5): (a) racemic sample; (b) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $2BF_4^-BAr_f^-$; (c) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $3BF_4^-$.

Dimethyl 2-(2-nitro-1-(pyridine-3-yl)ethyl)malonate (6fc).

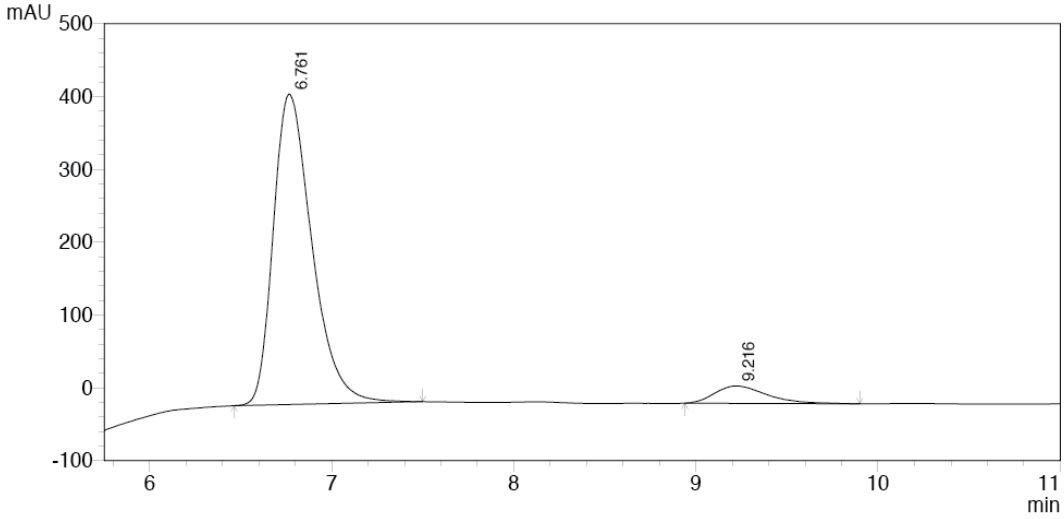
(a)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.803	3983767	230889	50.865	58.208
2	9.298	3848303	165770	49.135	41.792
Total		7832070	396659	100.000	100.000

(b)



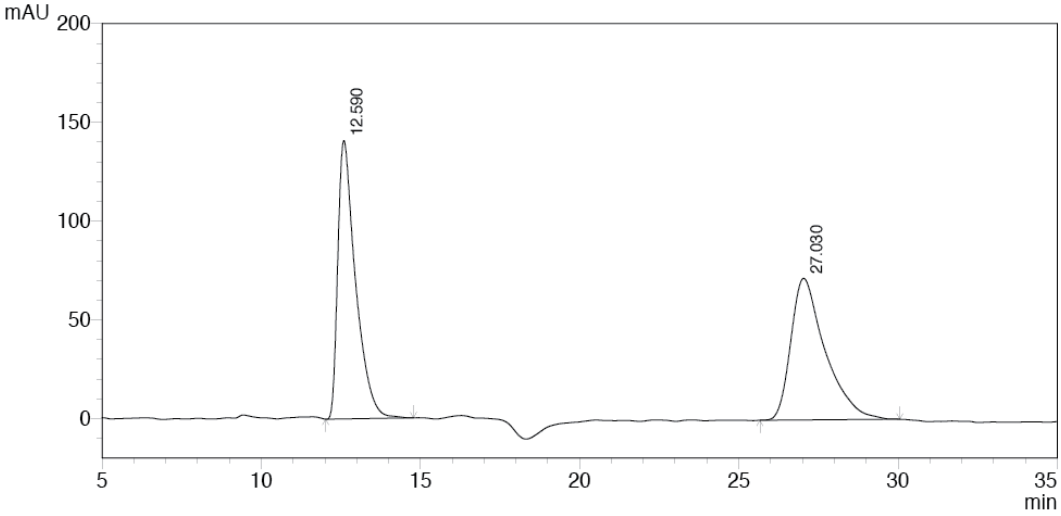
PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.761	6296885	426260	93.049	94.722
2	9.216	470397	23751	6.951	5.278
Total		6767282	450011	100.000	100.000

Figure s11. HPLC traces of **6fc** (Scheme 4, entry 6): (a) racemic sample; (b) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $2BF_4^-BAr_f^-$.

Dimethyl 2-(2-nitro-1-(2-trifluoromethylphenyl)ethyl)malonate (6gc).

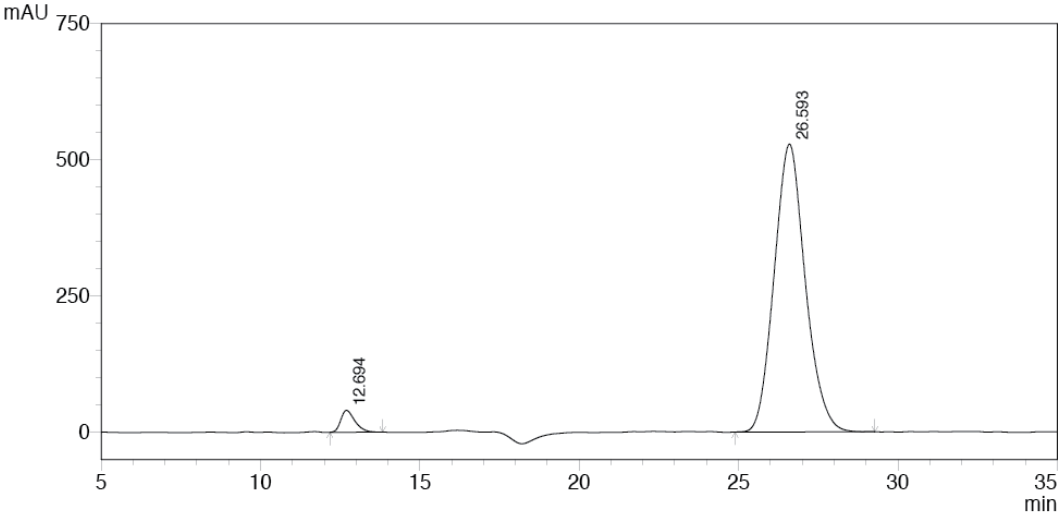
(a)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.590	5460013	141005	50.419	66.304
2	27.030	5369188	71660	49.581	33.696
Total		10829201	212664	100.000	100.000

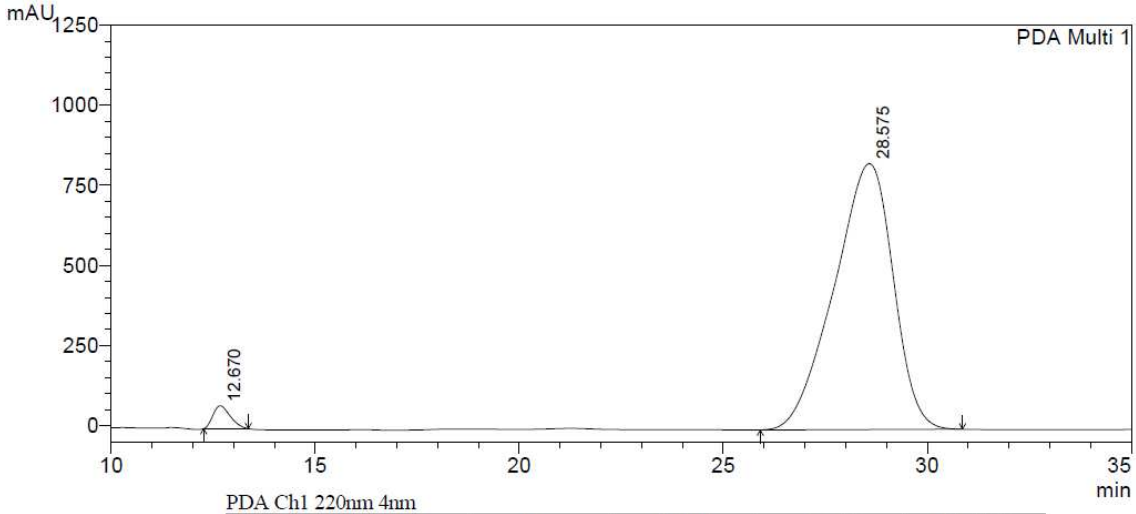
(b)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.694	1238157	40259	3.339	7.083
2	26.593	35848703	528088	96.661	92.917
Total		37086861	568347	100.000	100.000

(c)



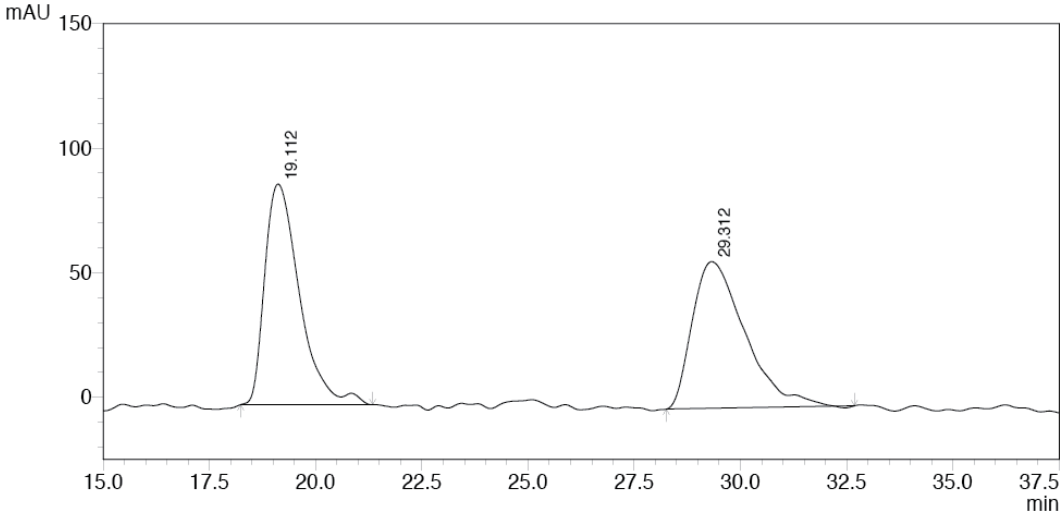
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.670	2106599	71450	2.458	7.929
2	28.575	83582140	829703	97.542	92.071
Total		85688739	901153	100.000	100.000

Figure s12. HPLC traces of **6gc** (Scheme 4, entry 7): (a) racemic sample; (b) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $2BF_4^-BAr_f^-$; (c) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $3BF_4^-$.

Dimethyl 2-(2-nitro-1-(2-acetoxyphenyl)ethyl)malonate (6hc).

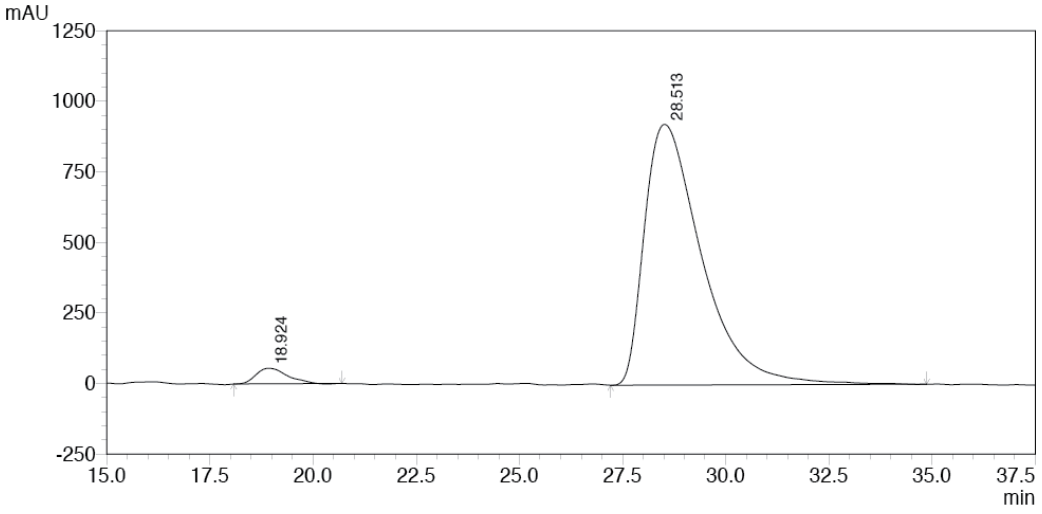
(a)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.112	5040868	88545	49.885	60.058
2	29.312	5064198	58886	50.115	39.942
Total		10105066	147431	100.000	100.000

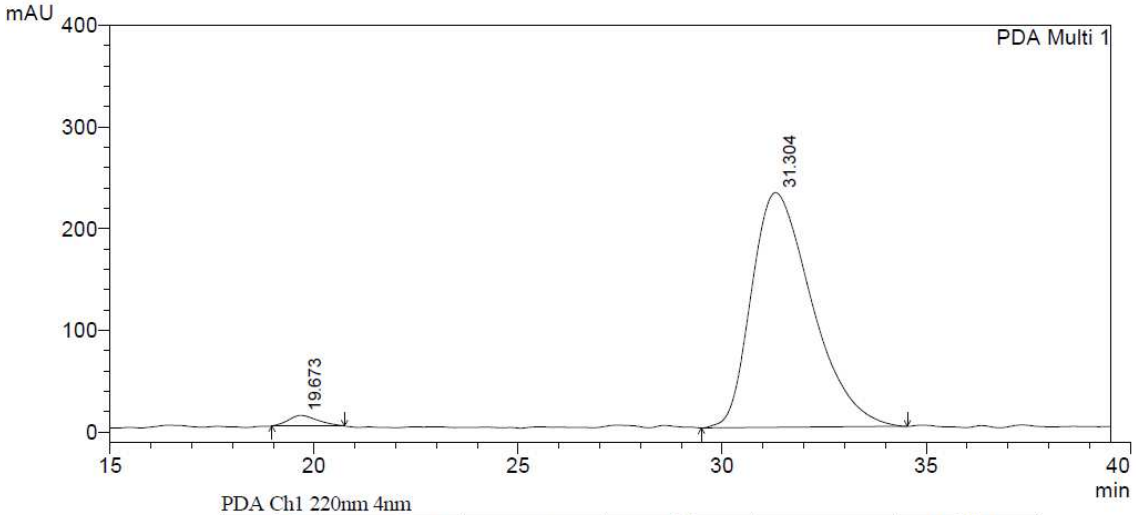
(b)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.924	2878634	55143	3.121	5.635
2	28.513	89360381	923530	96.879	94.365
Total		92239015	978673	100.000	100.000

(c)



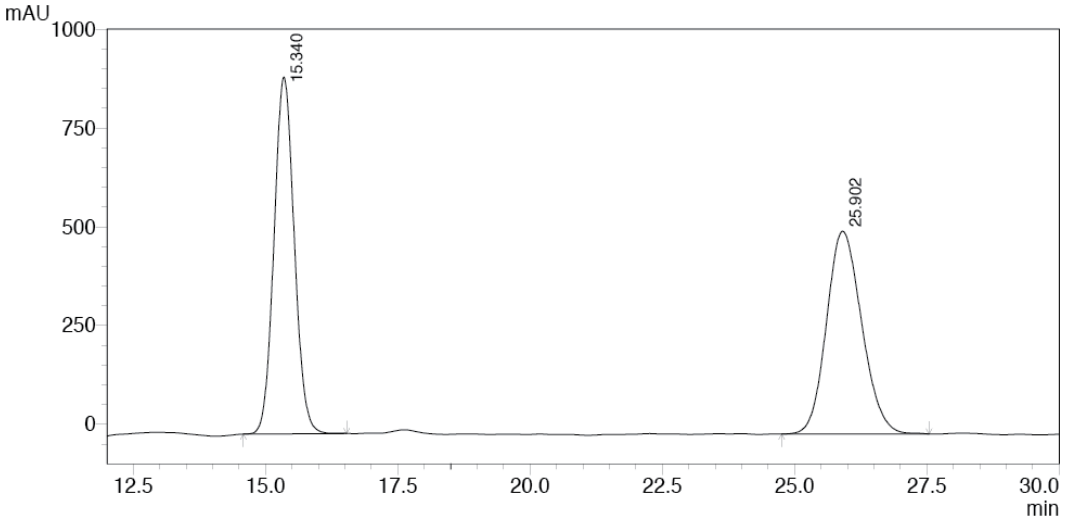
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.673	516825	10453	2.121	4.329
2	31.304	23852738	231012	97.879	95.671
Total		24369562	241465	100.000	100.000

Figure s13. HPLC traces of **6hc** (Scheme 4, entry 8): (a) racemic sample; (b) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $2BF_4^-BAr_f^-$; (c) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $3BF_4^-$.

Dimethyl 2-(2-nitro-1-(2-benzoyloxyphenyl)ethyl)malonate (6ic).

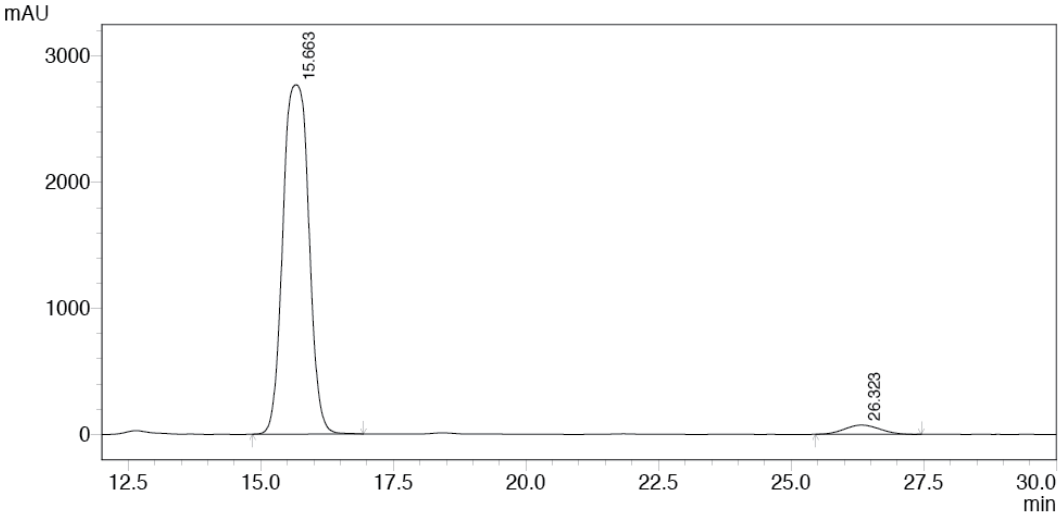
(a)



PDA220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.340	24105156	903431	50.293	63.762
2	25.902	23824081	513442	49.707	36.238
Total		47929237	1416873	100.000	100.000

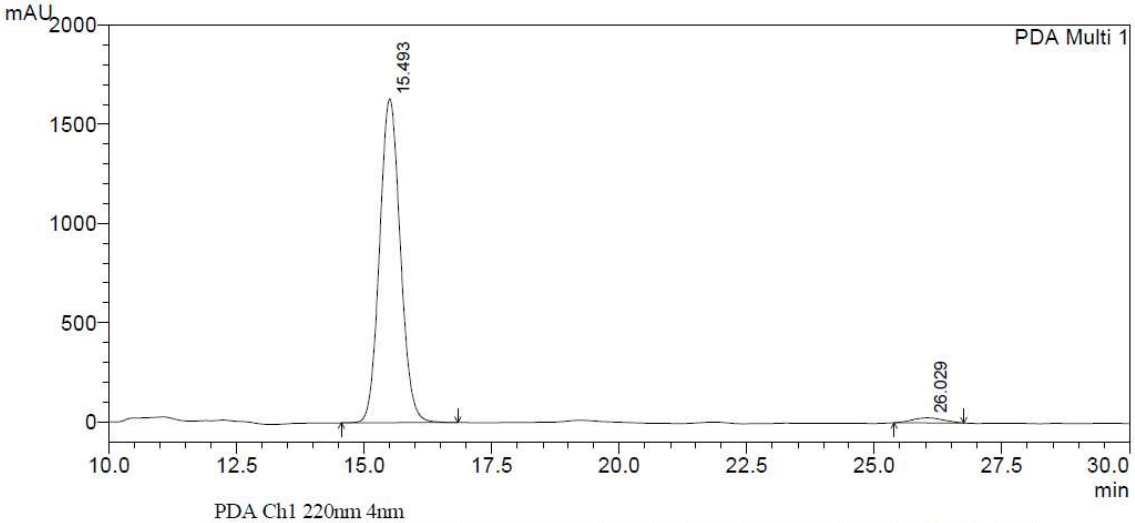
(b)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.663	94240443	2770460	96.556	97.428
2	26.323	3360915	73149	3.444	2.572
Total		97601359	2843609	100.000	100.000

(c)



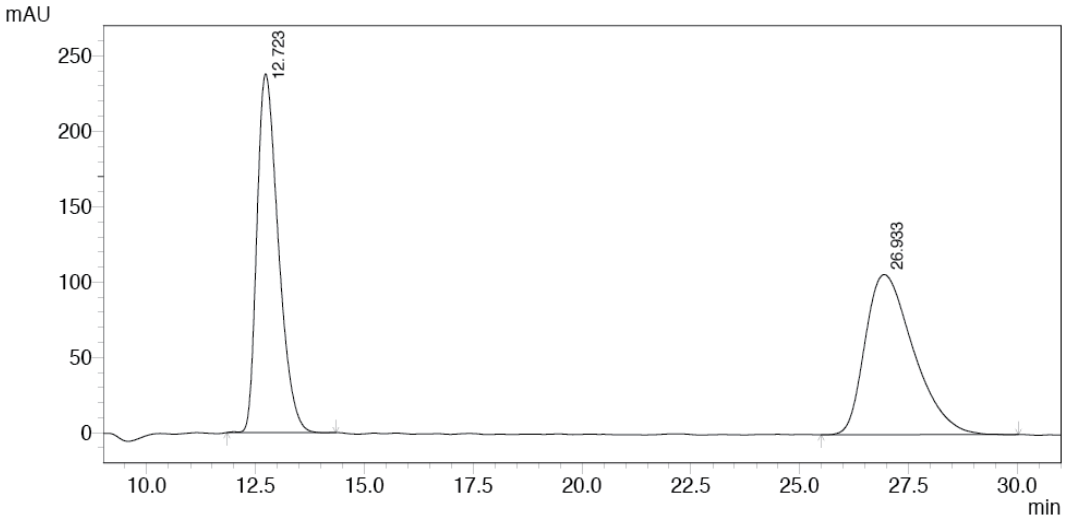
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.493	46134869	1632201	97.791	98.512
2	26.029	1042135	24649	2.209	1.488
Total		47177003	1656850	100.000	100.000

Figure s14. HPLC traces of **6ic** (Scheme 4, entry 9): (a) racemic sample; (b) catalyzed by Λ-(*S*,*S*)-**3**$^{3+}$ 2$BF_4^-$$BAr_f^-$; (c) catalyzed by Λ-(*S*,*S*)-**3**$^{3+}$ 3BF_4^-.

Dimethyl 2-(2-nitro-1-(2-benzyloxyphenyl)ethyl)malonate (6jc).

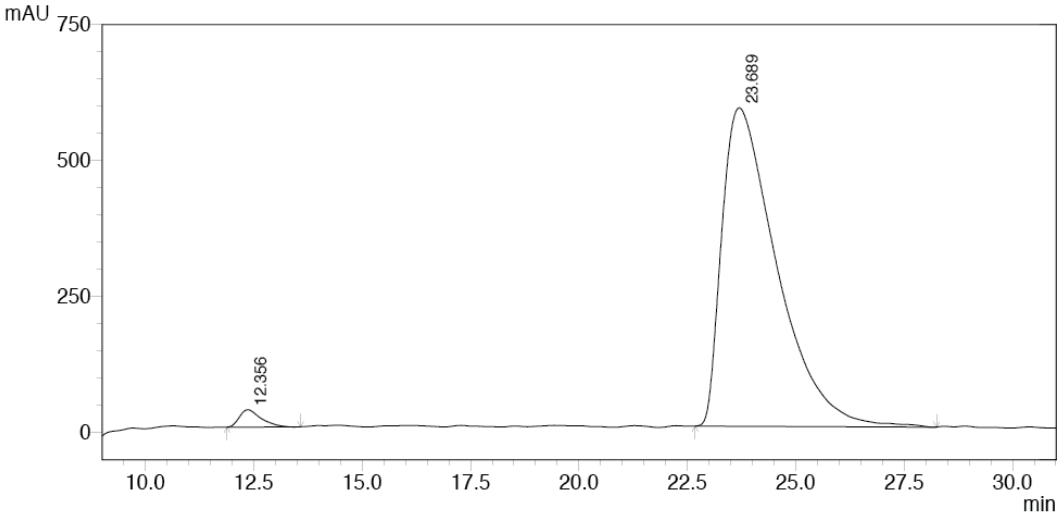
(a)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.723	8141200	238008	49.819	69.153
2	26.933	8200292	106170	50.181	30.847
Total		16341493	344178	100.000	100.000

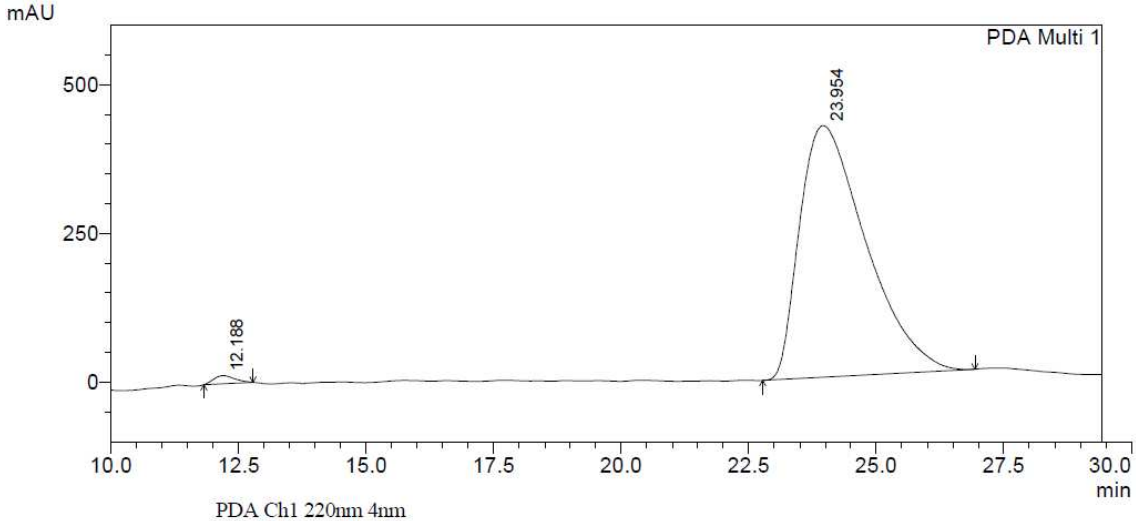
(b)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.356	1090049	31778	2.068	5.151
2	23.689	51627061	585142	97.932	94.849
Total		52717109	616920	100.000	100.000

(c)



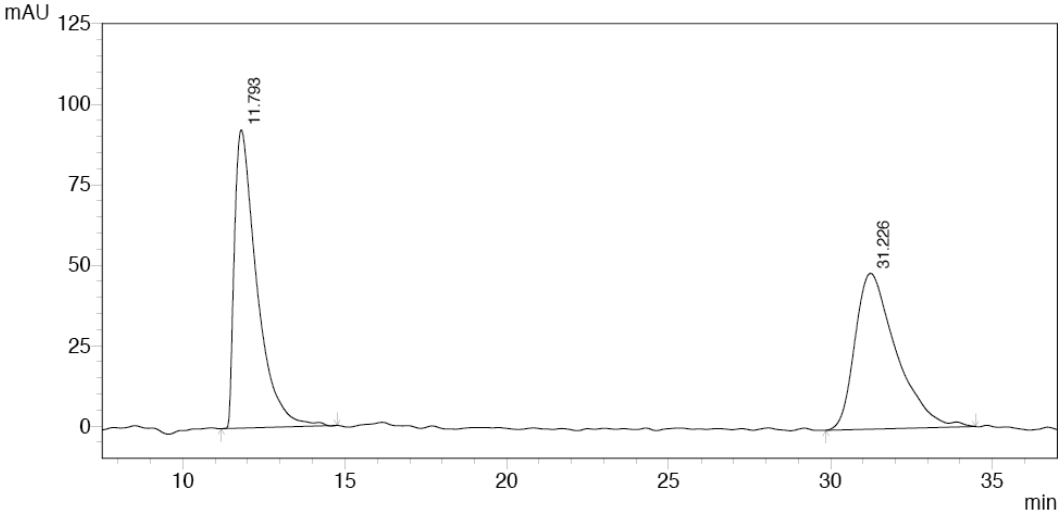
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.188	394877	13671	1.023	3.133
2	23.954	38205544	422701	98.977	96.867
Total		38600420	436372	100.000	100.000

Figure s15. HPLC traces of **6jc** (Scheme 4, entry 10): (a) racemic sample; (b) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $2BF_4^-BAr_f^-$; (c) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $3BF_4^-$.

Dimethyl 2-(2-nitro-1-furylethyl)malonate (6kc).

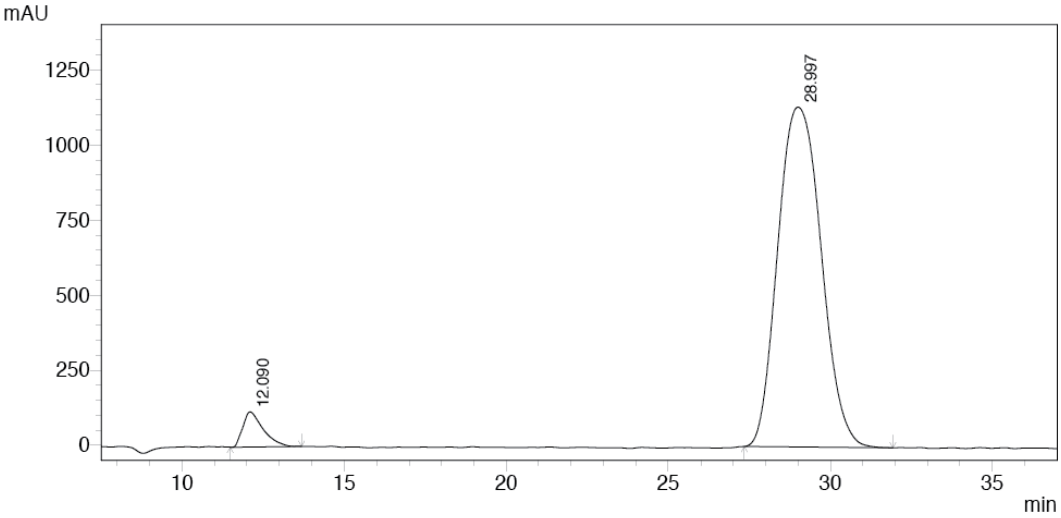
(a)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.793	4468208	92606	51.035	65.690
2	31.226	4287008	48367	48.965	34.310
Total		8755216	140974	100.000	100.000

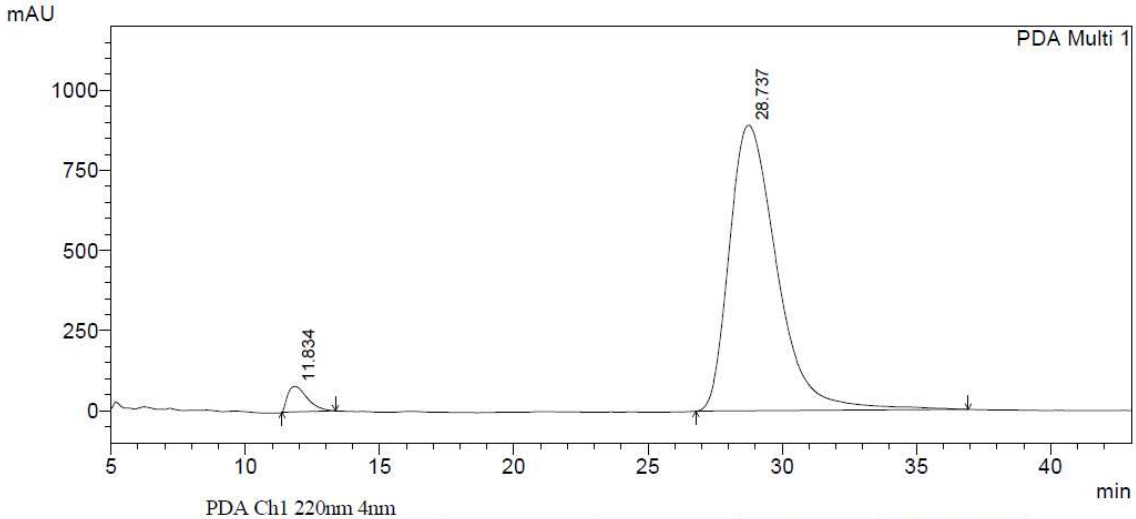
(b)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.090	5063370	116519	4.580	9.340
2	28.997	105482048	1131049	95.420	90.660
Total		110545419	1247568	100.000	100.000

(c)



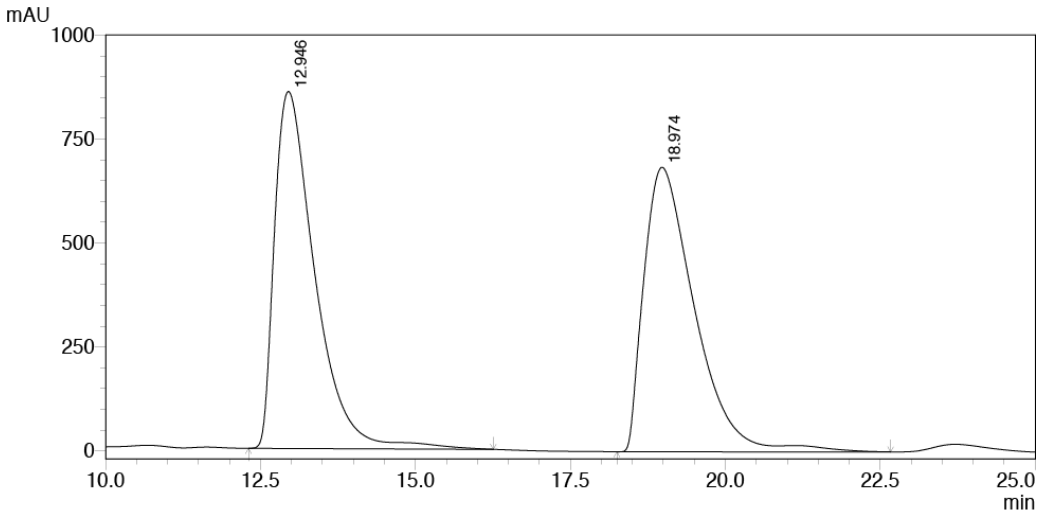
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.834	4048469	79205	3.554	8.165
2	28.737	109879149	890798	96.446	91.835
Total		113927618	970003	100.000	100.000

Figure s16. HPLC traces of **6kc** (Scheme 4, entry 11): (a) racemic sample; (b) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $2BF_4^-BAr_f^-$; (c) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $3BF_4^-$.

Dimethyl 2-(2-nitro-1-propylethyl)malonate (6lc).

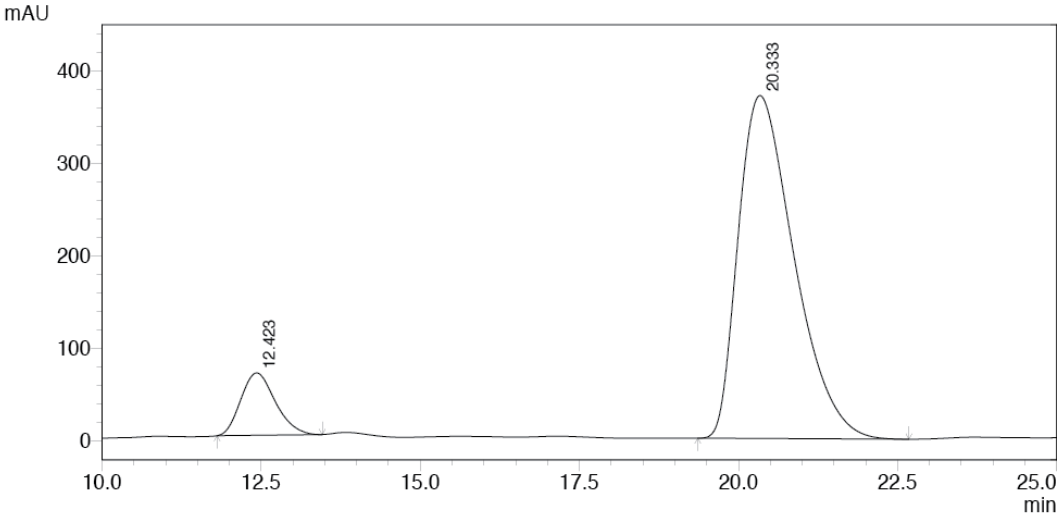
(a)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.946	38973226	858914	49.978	55.647
2	18.974	39007602	684601	50.022	44.353
Total		77980828	1543515	100.000	100.000

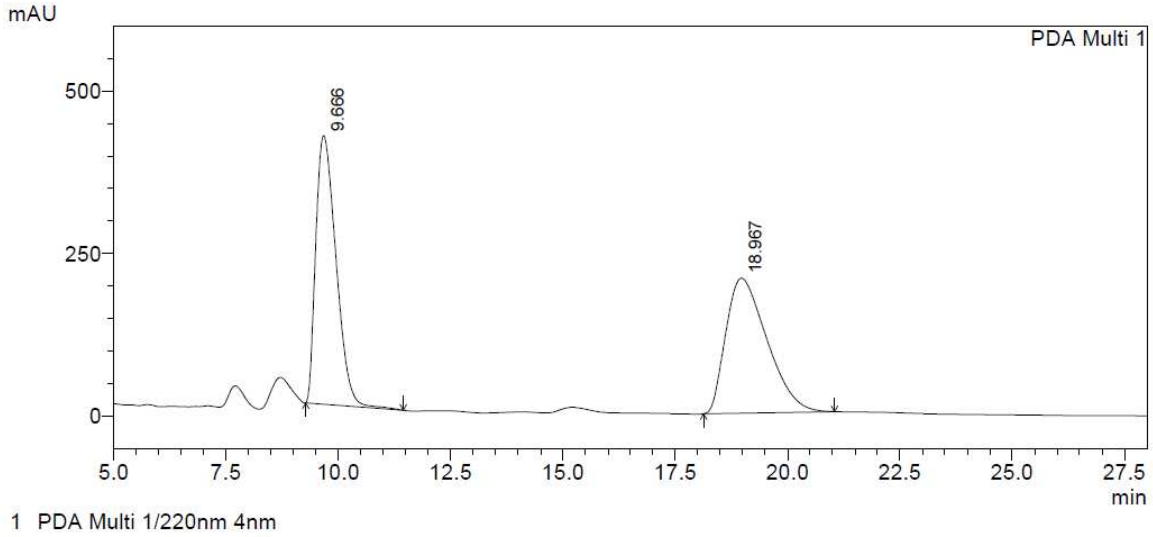
(b)



PDA 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.423	2538858	67307	10.100	15.379
2	20.333	22598513	370346	89.900	84.621
Total		25137371	437652	100.000	100.000

(c)



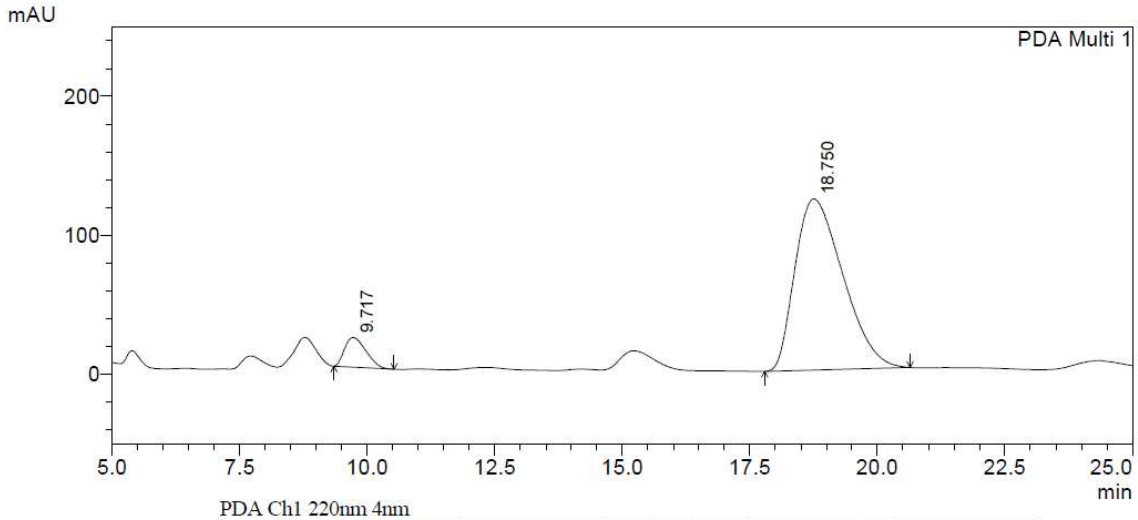
1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.666	12941031	413408	49.424	66.552
2	18.967	13242511	207771	50.576	33.448
Total		26183542	621179	100.000	100.000

(d)



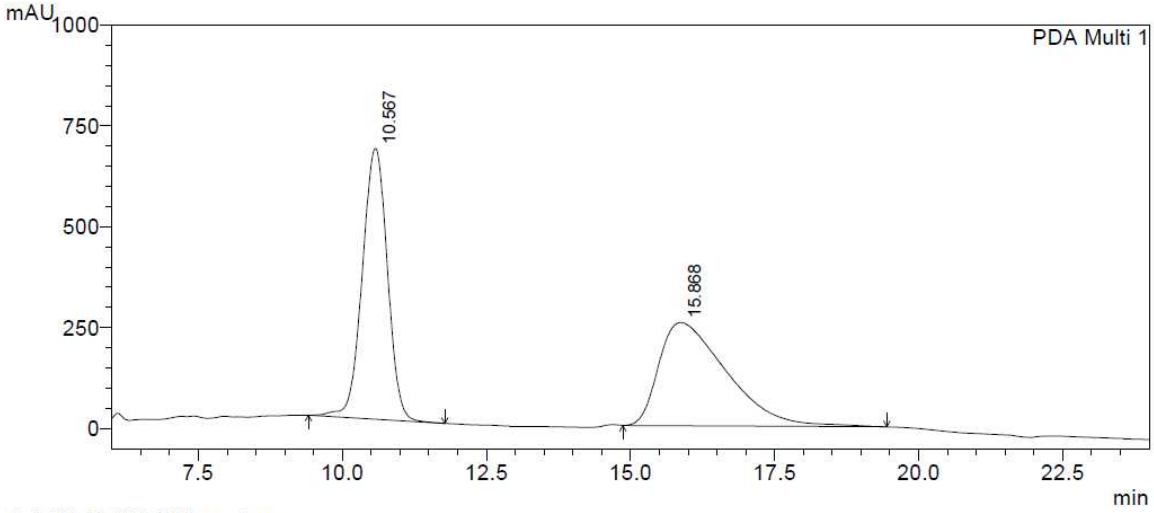
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.717	622512	21401	7.162	14.797
2	18.750	8069654	123232	92.838	85.203
Total		8692166	144634	100.000	100.000

Figure s17. HPLC traces of **6lc** (Scheme 4, entry 12): (a) racemic sample; (b) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $2BF_4^-BAr_f^-$ and analyzed per a; (c) racemic sample six months later (older column); (d) catalyzed by Λ-(*S*,*S*)-$\mathbf{3}^{3+}$ $3BF_4^-$ and analyzed per c.

***N,N′*-Bis(*t*-butoxycarbonyl)-1-hydrazino-2-oxocyclopentanecarboxylic acid ethyl ester (9a).**

(a)



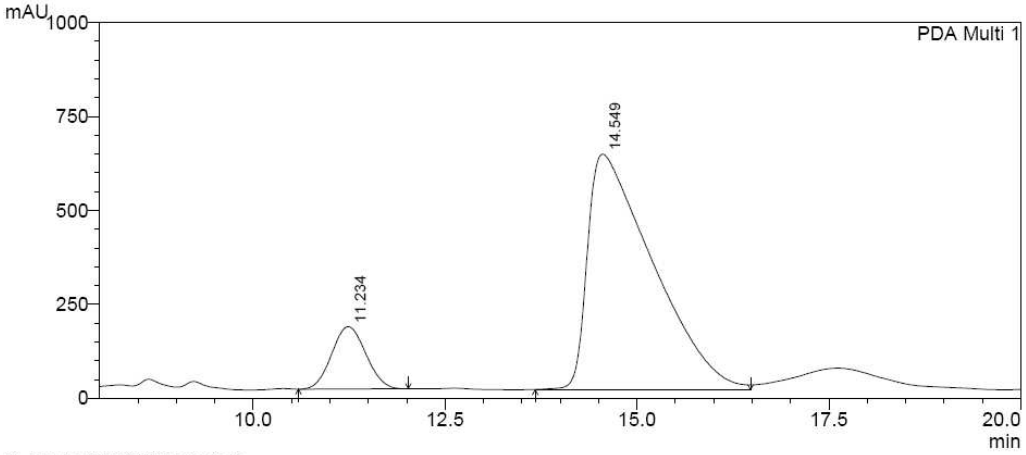
1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.567	20407922	671133	49.435	72.401
2	15.868	20874427	255836	50.565	27.599
Total		41282348	926970	100.000	100.000

(b)



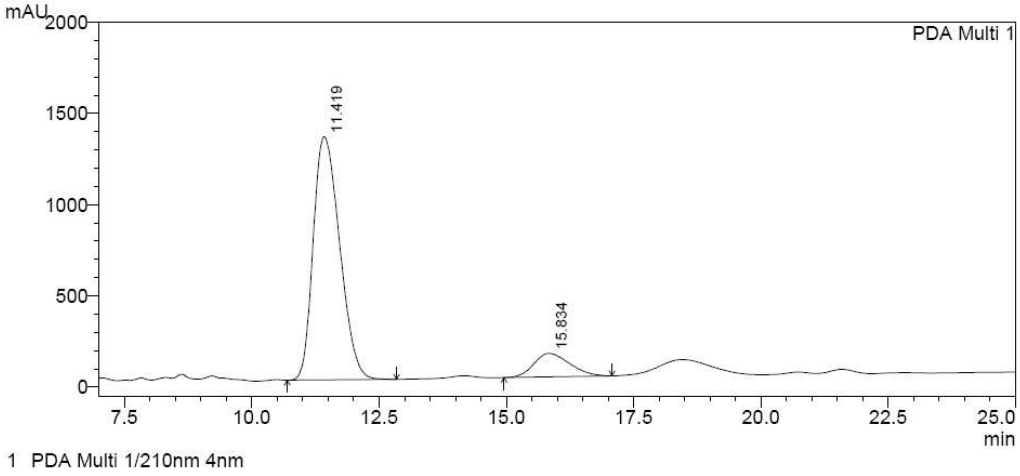
1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.234	5140005	165769	12.153	20.925
2	14.549	37155368	626417	87.847	79.075
Total		42295373	792186	100.000	100.000

(c)



PeakTable

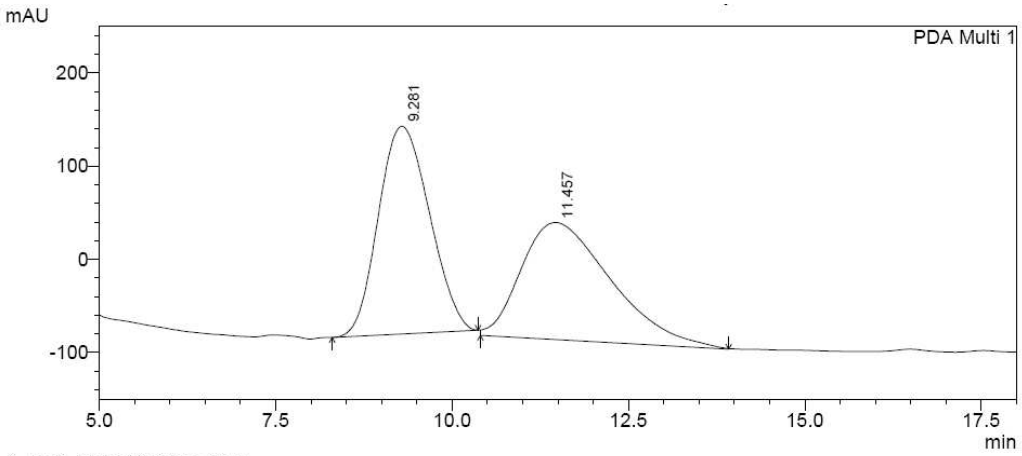
PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.419	48272755	1334808	88.385	91.220
2	15.834	6343733	128482	11.615	8.780
Total		54616488	1463290	100.000	100.000

Figure s19. HPLC traces of **9a** (Scheme 5): (a) racemic sample; (b) catalyzed by Λ-(*S*,*S*)-**3**$^{3+}$ 2Cl^{-}BAr$_f^{-}$; (c) catalyzed by Δ-(*S*,*S*)-**3**$^{3+}$ 2Cl^{-}BAr$_f^{-}$.

***N,N'*-Bis(*t*-butoxycarbonyl)-1-hydrazino-2-oxocyclohexanecarboxylic acid ethyl ester (9b).**

(a)



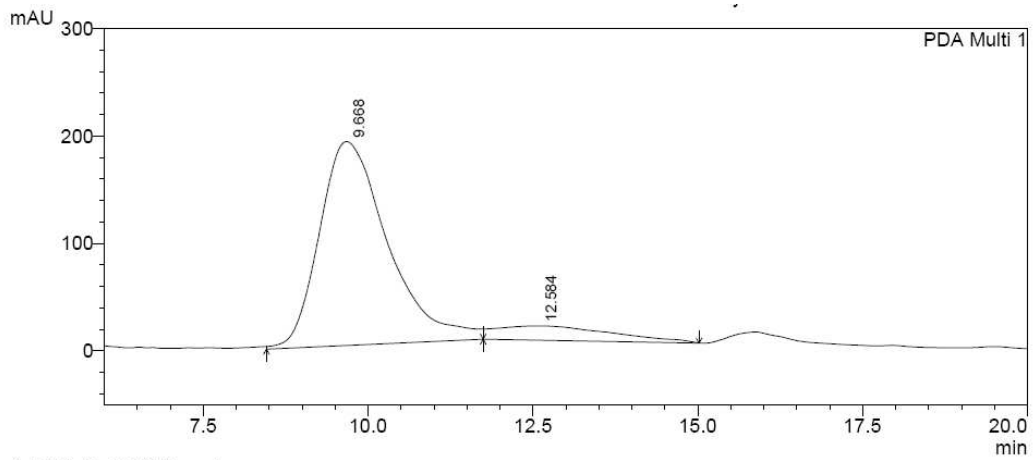
1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.281	11226181	222795	50.279	63.974
2	11.457	11101394	125466	49.721	36.026
Total		22327575	348261	100.000	100.000

(b)



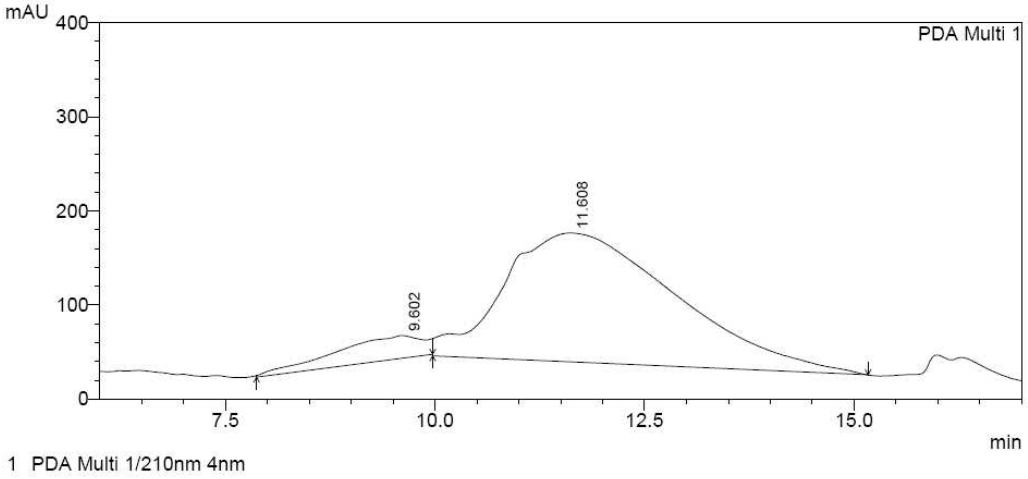
1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.668	13704382	189846	89.137	93.465
2	12.584	1670090	13274	10.863	6.535
Total		15374472	203120	100.000	100.000

(c)



PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.602	1940896	24296	8.979	15.067
2	11.608	19676191	136958	91.021	84.933
Total		21617087	161253	100.000	100.000

Figure s19. HPLC traces of **9b** (Scheme 5): (a) racemic sample; (b) catalyzed by Λ-(*S*,*S*)-**3**$^{3+}$ 2Cl^{-}BAr$_f^{-}$; (c) catalyzed by Δ-(*S*,*S*)-**3**$^{3+}$ 2Cl^{-}BAr$_f^{-}$.